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Bachelor Degree on Chemical and Biochemical Science Engineering

Improvement of the Manufacturing Process of a Novel Microfiltration Membrane

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Melhoramento do Processo de Fabrico de uma Nova Membrana de Microfiltração

Por:

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ABSTRACT

This thesis has the objective of studying and optimizing the manufacturing process of a novel microfiltration ceramic membrane technology, developed by Smart Separations Ltd (SSL), a start-up founded in July 2013 and based in London, UK. This patented microfiltration technology enables the manufacture of ceramic-based membranes with tailored conical pores to suit different needs, such as indoor air purification, emissions reduction, water purification and cell separations. SSL's platform technology allows the control of the pore size within the microfiltration range (0,1 to 50 μm). Besides its on-demand micron-sized pores, this patented process allows the production of membranes with outstanding properties, including its unique anti-clogging pore geometry, high porosity, mechanical and chemical strength, thermal stability and reusability.

The study comprised in this thesis focuses on one of the stages of the manufacturing process of SSL ceramic membranes: the casting process, or its green-body formation. During casting, the initial dope mixture (composed of ceramic particles, a dispersant, an organic solvent and a polymer) comes into contact with a non-solvent and solidifies, through a process termed phase-inversion. In order to achieve a high quality product, it is critical that from this stage a flat, pattern-free membrane is created. With this objective in mind, the first step was the elimination of the human error, with the implementation of an automatic casting solution submersion apparatus. This method was optimized, reaching a suitable submersion velocity (2,7 cm/sec).

From here, it was also understood that the material of the casting mould could also play a role in the quality of manufacturing. Therefore, the material of construction of the casting mould was also subject of study during this project. With the objective of selecting the most suitable casting material to be used in the manufacturing process, membranes were casted and characterized in terms of bending, flatness, existence of wavy patterns and microstructure. Material A was the material that achieved the best outcome.

The dope's milling and mixing times were also studied. Suspensions with different combinations of milling and mixing times were casted, in order to understand the impacts of these times on the manufacturing process. However, no conclusions were possible to make from this experiment and therefore future work to better understand this influence is proposed.

Keywords: ceramic membrane, microfiltration, manufacturing process, membrane casting, phase-inversion and microstructure.

RESUMO

Esta dissertação tem como objetivo o estudo e a otimização do processo de produção de uma inovadora membrana cerâmica de microfiltração, desenvolvida pela *Smart Separations Ltd (SSL)*, uma *start-up* fundada em Julho de 2013 e sediada em Londres, Reino Unido. Esta tecnologia de microfiltração patenteada permite a produção de membranas cerâmicas com poros cónicos "feitos à medida" para diferentes aplicações, tais como a purificação de ar dentro de edifícios, a redução de emissões, a purificação de água ou a separação de células. A tecnologia desenvolvida pela *Smart Separations* possibilita o controlo do tamanho de poros dentro da gama de microfiltração (0,1 a 50 μm). Além de membranas com poros "feitos à medida", este processo patenteado proporciona a produção de membranas com excelentes propriedades, tais como a elevada porosidade, a resistência física e química, a estabilidade térmica e a possibilidade de reutilização.

O estudo apresentado nesta tese tem como foco uma das etapas do processo produtivo das membranas da SSL: o processo de moldagem. Durante este processo, a mistura (composta por partículas cerâmicas, um dispersante, um solvente orgânico e um polímero) entra em contato com um não-solvente e solidifica, através de um processo denominado de "inversão de fase". De modo a obter um produto de elevada qualidade, é crucial que durante esta etapa do processo de produção se consiga obter uma membrana perfeitamente plana. Com este objetivo em mente, o primeiro passo foi a eliminação do erro humano, através da implementação de um sistema automático de submersão da solução a moldar. Este método foi otimizado e chegou-se a uma velocidade ótima de submersão (2,7 cm/s).

Deste estudo, foi também concluído que o material do molde usado para a submersão da solução a moldar tinha um papel fundamental na qualidade do produto final. Posto isto, o material do molde usado foi também sujeito a testes. Com o objetivo de selecionar o material mais adequado para este processo, várias membranas foram fabricadas e caraterizadas de acordo com a sua curvatura, a existência de padrões ondulados e a sua microestrutura. O material A foi o material que proporcionou melhores resultados.

As durações da moagem e da mistura da solução também foram estudadas. Suspensões com diferentes combinações de tempos de preparação foram moldadas, de modo a perceber qual é o impacto da variação da sua duração no processo produtivo. No entanto, nenhumas conclusões foram retiradas deste último estudo, sendo propostas experiências futuras neste sentido.

Palavras-chave: membranas cerâmicas, microfiltração, processo de produção, inversão de fase e microestrutura.

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Abbreviations / Nomenclature

Abbreviation	Definition
Ca	Calcium
CA	Cellulose Acetate
D	Dialysis
DIPS	Diffusion Induced Phase Separation
GP	Gas Permeation
MF	Microfiltration
Mg	Magnesium
NF	Nanofiltration
PV	Pervaporation
RO	Reverse Osmosis
SOP	Standard Operating Procedure
SSL	Smart Separations Ltd
TIPS	Thermally Induced Phase Separation
UF	Ultrafiltration

1

INTRODUCTION

1.1 Framework of this Research Work

The process industries produce a wide variety of chemicals and components that present the manufacturer with a need for separation, concentration and purification. Membrane science and technology is an expanding field and has become a prominent part of many industrial processes.
The global filtration market comprises a wide range of filtration, separation and purification products. Although molecular and macro level filtrations are widely used, the filtration of small particles or microorganisms (microfiltration) appears at a very challenging middle.
So far, two different approaches have been tried to close this gap. By opening the pores of a polymeric membrane used for molecular filtration it is possible to reach the microfiltration range. However, these membranes only withstand pores larger than 1 μm at the expense of integrity and cost. On the other hand, the top-down approach consists on reducing the size of the sieves used to separate larger particles. Nevertheless, achieving pore sizes below 100 μm is a task only available to very expensive technologies, such as lithography imprinting. (Smart Separations Ltd, s.d.)
This dissertation was developed with the intent of help closing this technological gap, by improving the manufacturing process of a novel microfiltration membrane, developed by Smart Separations Ltd.

1.2 The Company

Founded in July 2013, Smart Separations is a limited company based in London, United Kingdom. As of this moment, the company is composed of 8 team members with different backgrounds, providing the know-how in both business and research environments needed to the company's development. To complement this multidisciplinary team, a strong Scientific Advisory Board further improves Smart Separations' product development and market reach.

SSL's ambition is to be the world's leader in microfiltration and particle separation technology – filling the void gap that exists in the market nowadays. To do so, it has patented an innovative microfiltration technology to produce ceramic filters with self-assembled controllable pores of uniform size in the range between <1 and 50 μm.

The need to separate particles within this range is spread throughout several market segments where microfiltration is either already in use or can potentially be used. These include indoor air purification, emissions reduction, cell separations, wastewater treatment, blood processing, food, beverage, pharmaceutics, research, dairy industry and so forth. Reaching to all this market, Smart Separations is on track to fulfil its mission: "Improve quality of life trough innovation". (Smart Separations Ltd, s.d.)

1.3 Smart Separations' Technology

Smart Separations has developed a filter in the microfiltration range (1 to 50 μm in diameter, or around the thickness of a human hair). The combination of micro-patterning and controlled abrasion of a ceramic support enables the creation of a unique filter with tailored "flared" or "conical" pore sizes to suit different needs, high pore density and good mechanical. With fabrication costs significantly lower than rival technologies, these unique selling points are complemented by a structure that is sterializable, recyclable and reusable – all important conditions for mainstream applications. Moreover, its rigid structure and stability at high temperatures (over 1,000ºC) allows structured modifications that would otherwise be impossible to achieve with polymeric membranes. This brings further benefits to attract other markets and applications, such as with the development of a novel microfiltration membrane with electrically-conductive properties or coated with active chemical molecules.

1.4 Thesis Research Objectives

The main objective of this dissertation is the improvement of the manufacturing process of a ceramic microfiltration membrane, with focus on the casting stage. Membrane casting, through the phase-inversion process, is one of the many steps on the production of ceramic membranes. It precedes the sintering and lapping steps, making its good implementation and optimization imperative.

During this process, the membranes should remain flat, without patterns on its surfaces, and the phase-inversion should be achieved without any issues, so that the self-assembled microstructure is properly formed. The flatness of the membrane is extremely important to maintain a low pore size distribution, in order to attain an efficient particle separation throughout the membrane.

In order to achieve this goal, specific objectives were considered:

- Implementation and optimization of an automatic casting solution submersion apparatus (dipper);
- Study of different methods to protect the dope's top surface during submersion;

- Study of the material of construction of the casting mould;
- Determination of the most suitable material and design to be used on the casting moulds;
- Study of the dope's milling and mixing times;
- Implementation of a standard operating procedure for casting of Smart Separations' membranes.

To scale-up the Smart Separations' membranes manufacturing, this process must be understood, planned and optimized, eliminating the variability and inefficacy of the procedure.

1.5 Thesis Outline

Beyond the present introduction, this dissertation includes five other chapters.

In chapter 2, a literature review of membrane technology and membrane casting is made, emphasizing topics such as microfiltration processes, ceramic membranes, and phase-inversion.

The manufacturing process of Smart Separations if explained in chapter 3, highlighting its four stages: dope mixing, membrane casting, sintering and lapping.

Chapter 4 comprises the methods and equipment used throughout this research work.

Chapter 5 includes the results obtained in the experiments and its discussion.

Finally, in chapter 6 the main conclusions of this study are stated and proposals for future work to study and improve the manufacturing process are presented.

2

LITERATURE REVIEW

2.1 Membrane Technology

A membrane can be defined as a barrier used to separate two phases and that is capable to contain the transport of various component in a selective manner. The term "filter", which has the same purpose as a membrane, is usually applied in separations where the particles in suspension are larger than 1-10 μm. (Wang, Chen, Hung, & Shammas, 2011)

In a membrane separation process, a feed consisting of a mixture of two or more components is separated into a retentate (portion of the feed that is retained by the membrane) and a permeate (part of the mixture that pass through the membrane). A general membrane process is shown in Figure 2.1, with an optional sweep used to help remove the permeate. (Seader & Henley, 1997)

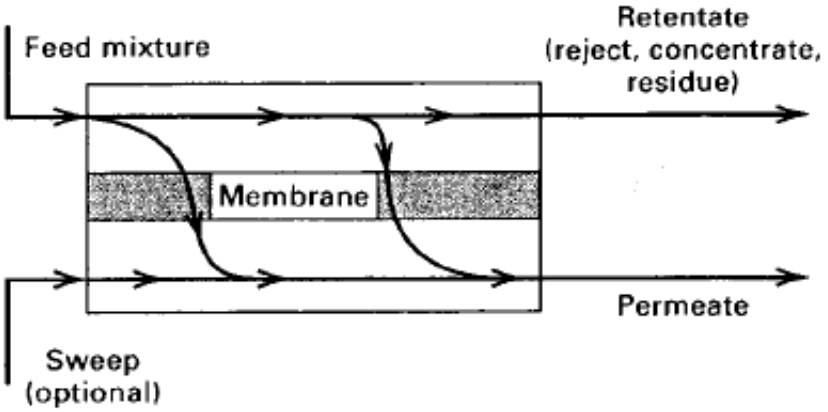


Figure 2.1 - General membrane process (Seader & Henley, 1997)

When compared to other separation processes such as distillation, absorption or evaporation, membrane filtration can provide many advantages. Their compactness, ease of fabrication, operation and modular design make them suitable and attractive for many industrial applications. Since the use of heat is not usually required, the use of membrane separations is a considerable energy saving, when compared to conventional processes. This also means that no complicated heat transfer or heat generating equipment is needed, making the process easier and cleaner to operate. (Nath, 2017)

According to the driving force applied, the membrane processes can be classified as pressure driven processes, concentration gradient driven process (such as dialysis), temperature driven

processes (such as membrane distillation) or electrical potential driven processes (such as electrodialysis). (Wang, Chen, Hung, & Shammas, 2011)

2.1.1 Pressure Driven Membrane Processes

Pressure is the most common driving force applied and its processes can be further classifies according to particle size in 4 categories: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. An overview of these processes can be observed on Table 2.1.

Table 2.1 - Overview of pressure driven membrane processes and their characteristics (Bruggen, Vandecasteele, Gestel, Doyen, & Leysen, 2003) (Mulder, 1996) (WO Patente Nº WO2005058465 A2, 2005)

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Permeability (l/h.m^2.bar)	>50	10 – 50	1,5 – 30	0,05 – 1,5
Pressure (bar)	0,1 – 2	0,1 – 5	3 – 20	5 – 120
Pore size (nm)	100 – 100 000	2 – 100	0,5 – 2	<0,5
Rejection				
• **Monovalent ions**	-	-	-	+
• **Multivalent ions**	-	-/+	+	+
• **Small organic compounds**	-	-	-/+	+
• **Macromolecules**	-/+	+	+	+
• **Particles**	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving Charge effects	Solution - Diffusion
Membrane morphology	Porous	Porous	Porous/Dense	Dense

2.1.1.1 Microfiltration

Microfiltration is a filtration technique widely used in the concentration, purification or separation of macromolecules, colloids and suspended particles from solution. MF membranes have nominal pore sizes on the order of 0,1-100 μm and are usually operated at relatively low pressures in a cross-flow configuration, in order to prevent cake formation and hence fouling of the membrane. As the membrane retains suspended particles, the permeate flux decreases and the pressure drop increases. A typical pressure drop/filtration time curve can be observed in the Figure 2.2. When the filter becomes too clogged for effective use, the membrane must be cleaned or changed. (Charcosset, 2012) (Surtherland, 2008)

The accumulation of cells, debris and other rejected particles on the membrane surface (external fouling) is generally reversible, however deposition and adsorption of small particles and macromolecules within the pores can occur (internal fouling) and is often irreversible. (Charcosset, 2012)

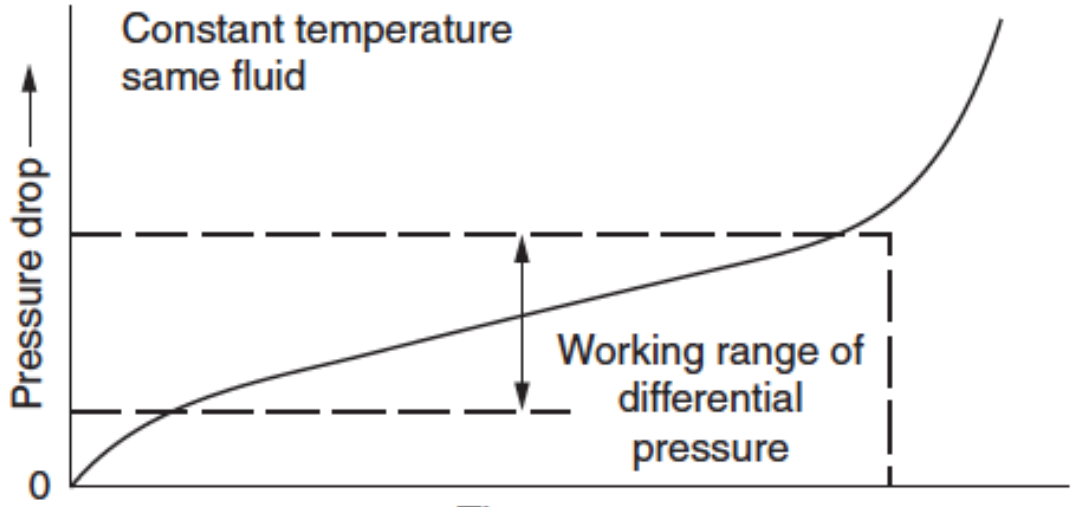


Figure 2.2 - Increase of pressure drop over filtration time (Surtherland, 2008)

MF membranes have high pore densities, hence its high flow rates. However, the irregularity nature of the pores and particles being filtered, mean there is not a precise cut off size during the process. Therefore the use of asymmetric membranes (which have narrower surface pore sizes compared with the bulk of the membrane) have been introduced, providing a sharp cut off size without compromising the high flow rate. (Scott & Hughes, 1996)

This separation process can be used in a wide range of applications such as in the removal of particles form liquid and gas streams for chemical, biological, pharmaceutical and food industries, in the clarification and sterile filtration of heat sensitive solutions and beverages, in the production of pure water in the electronics industry and in the waste water treatment. (Scott & Hughes, 1996) MF major applications are summarised in the Figure 2.3.

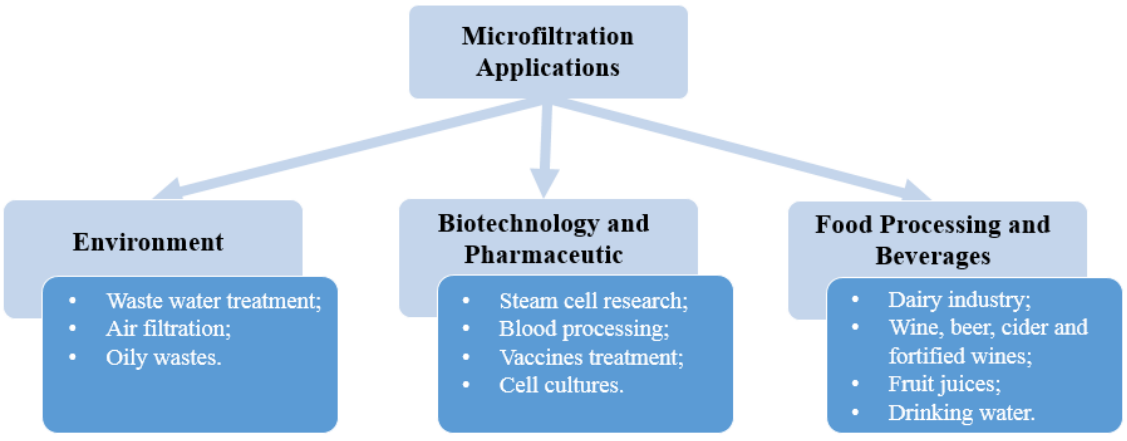


Figure 2.3 - Applications of microfiltration membranes (Azevedo, 2016)

2.1.1.2 Ultrafiltration

Ultrafiltration covers most of the region filtration between MF and RO. Solvents and salts of low molecular weight will pass through the membranes, whilst larger molecules are retained. UF membranes are asymmetric, 0,1-1 μm thick, of fine porous texture exposed to the feed side. These membranes are supported on a highly porous layer 50-250 μm thick, providing a combination of high permeability and permselectivity. Ultrafiltration is typically applied in the separation of macromolecular solutes and colloidal material from macromolecular solutes and solvents. There are many analytical applications on the laboratory scale, such as the concentration of proteins, enzymes, hormones, etc. and in biochemical and clinical analysis. UF membranes are used in several industries: chemical and nuclear (in the treatment of waste water and effluents), automobile (for recovery and recycling in electropaint baths), pulp and paper, food and diary (for the clarification of juices and wines, milk concentration sterile filtration, etc.), and biological and pharmaceutical (for the manufacture of antibiotics, removal of pyrogens and the treatment of blood and plasma). (Scott & Hughes, 1996)

2.1.1.3 Nanofiltration

Nanofiltration is a pressure driven process that operates between the separation capabilities of RO and UF membranes, that is in the separations of ions from solutes such as small molecules of sugars. NF is mostly used in food and biotechnology industries, for example, when high sodium rejection (typical of RO) is not needed but where other multivalent salts (such as Mg and Ca) are to be removed. (Scott & Hughes, 1996)

2.1.1.4 Reverse Osmosis

Reverse osmosis is a pressure driven process used to separate ionic solutes and macromolecules from aqueous streams. By applying enough pressure to exceed the osmotic pressure, the flow of water can occur from a more concentrated solution to a dilute solution. The membranes used in RO are either asymmetric or composite which typically have a <1 μm thick, dense top layer supported by a 50-150 μm thick porous sublayer. These membranes are applied in a wide range of applications such as: desalination of brackish water and sea water, production of pure water for a variety of industries, concentration of solutions of food products, pharmaceutical solutions and chemical streams, and waste water treatment. (Scott & Hughes, 1996)

2.1.2 Membrane Classification

There are many ways to classify membranes: they can be natural or synthetic, organic or inorganic, neutral or charged, porous or dense, its structure can be homogeneous or heterogeneous. (Wang, Chen, Hung, & Shammas, 2011)

Figure 2.4 schematises the membrane classification based on 4 different aspects: its nature, separation regime, geometry and internal structure.

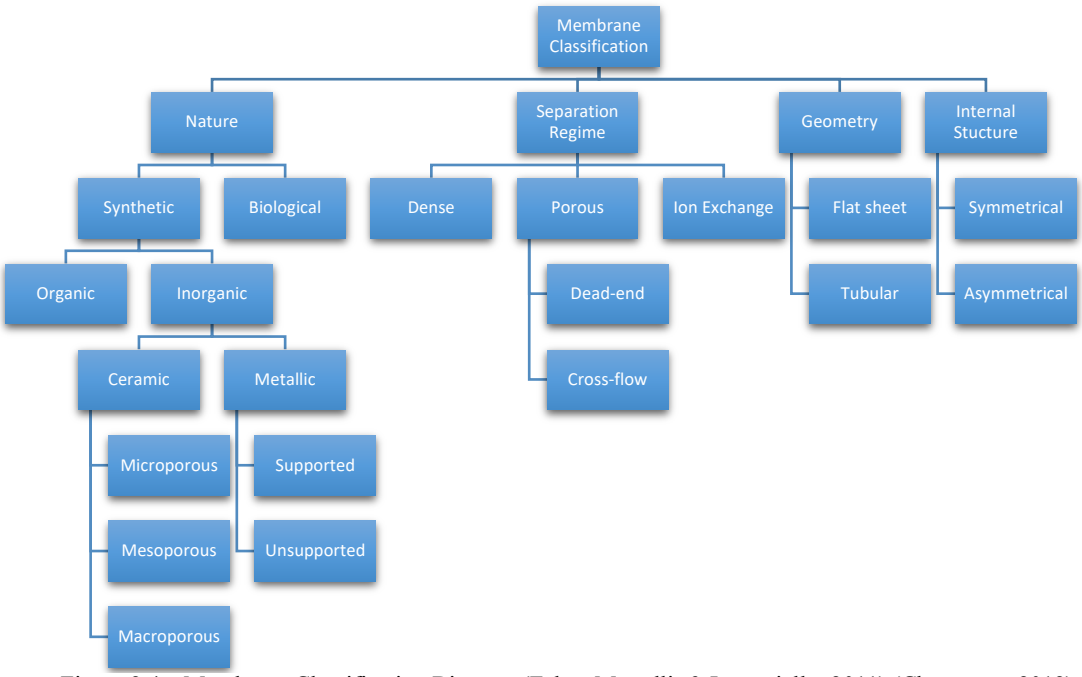


Figure 2.4 – Membrane Classification Diagram (Falco, Marrelli, & Iaquaniello, 2011) (Charcosset, 2012)

2.1.2.1 Nature

Regarding the nature of the membranes, they can be biological or synthetic. Biological membranes are easy to be manufactured, however they are not capable of withstanding high temperatures (above 100ºC), they have a narrow pH range of operation, problems associated to the clean-up and they are susceptible to microbial attachment due to their natural origin. (Falco, Marrelli, & Iaquaniello, 2011)

On the other hand, synthetic membranes can be subdivided into organic and inorganic. Organic membranes (polymeric) commonly operate between 100 and 300ºC, while ceramic and metallic membranes withstand temperatures above 200ºC, making them more appealing for industrial applications (despite its higher costs). (Falco, Marrelli, & Iaquaniello, 2011)

2.1.2.2 Separation Regime

A further membrane classification is based on the separation regime. In a dense membrane, the transport of components involves a stage of dissolution and diffusion across the membrane's material. When the transport occurs preferentially in the continuous fluid phase which fills the membrane pores, the membrane is denominated as porous. Lastly, if the separation is due to the difference in charge of the species to be separated, the membrane is classified as ion-exchange. (Charcosset, 2012)

In a porous membrane, the most widely used process is the dead-end or in-line filtration, where the entire feed is forced through the membrane under pressure. The equipment required for dead-end filtration is simpler but it requires constant cleaning or replacement. In cross-flow systems, the feed flows across the surface of the membrane, producing a particle-free permeate that crosses through the membrane and a retentate solution rich in particles. The equipment needed for this filtration is more complex but the membrane has a longer lifetime since the pores do not get clogged so often. These process are illustrated in the Figure 2.5. (Baker, 2004)

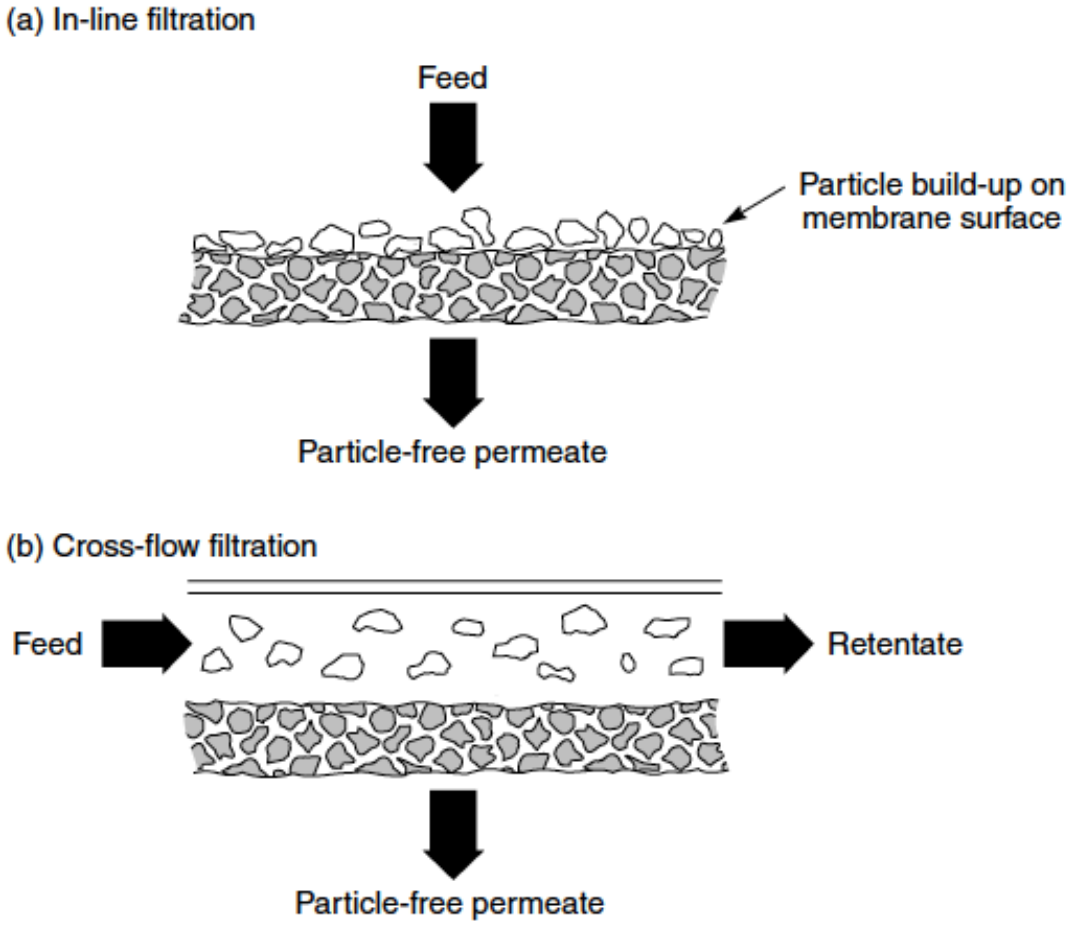
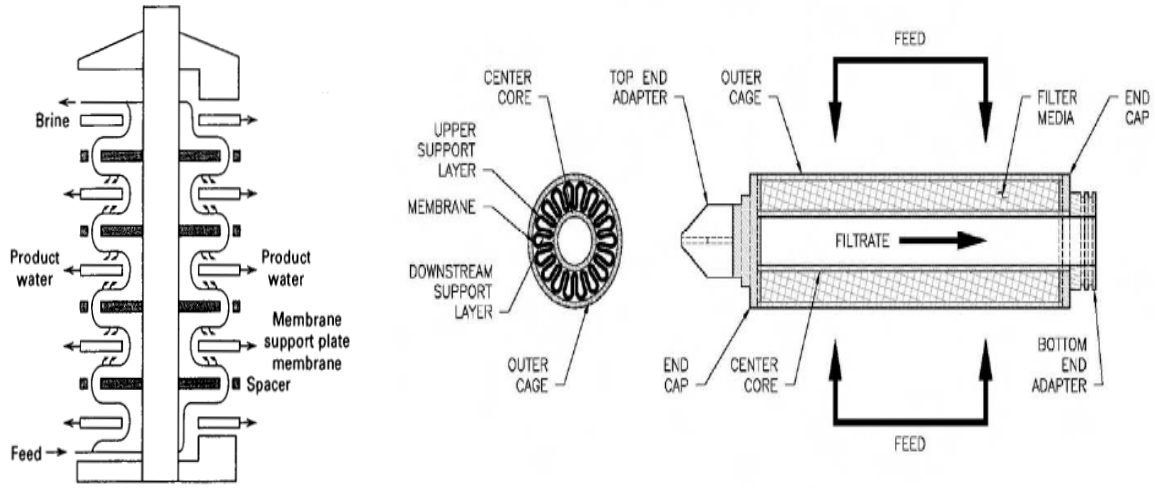


Figure 2.5 – Schematic representation of (a) in-line (or dead-end) filtration and (b) cross-flow filtration (Baker, 2004)

2.1.2.3 Geometry

According to its geometry, membranes can be available in 2 different shapes: flat sheet or tubular.

Flat sheet membranes are usually arranged in plate and frame modules, where as many as 100 membrane sheets are stacked into one equipment. Flat sheets used in plate and frame modules are circular, square or rectangular in cross-section. Support plates divide the membrane sheets and channel the permeate. Flat sheets can also be manufactured to assemble membrane cartridge filters, placing the sheets between a feed and a filtrate support layer, folding the membranes to increase its surface area within the cartridge. Both of these modules can be observed in Figure 2.6. (Seader & Henley, 1997) (United States Environmental Protection Agency, 2005)

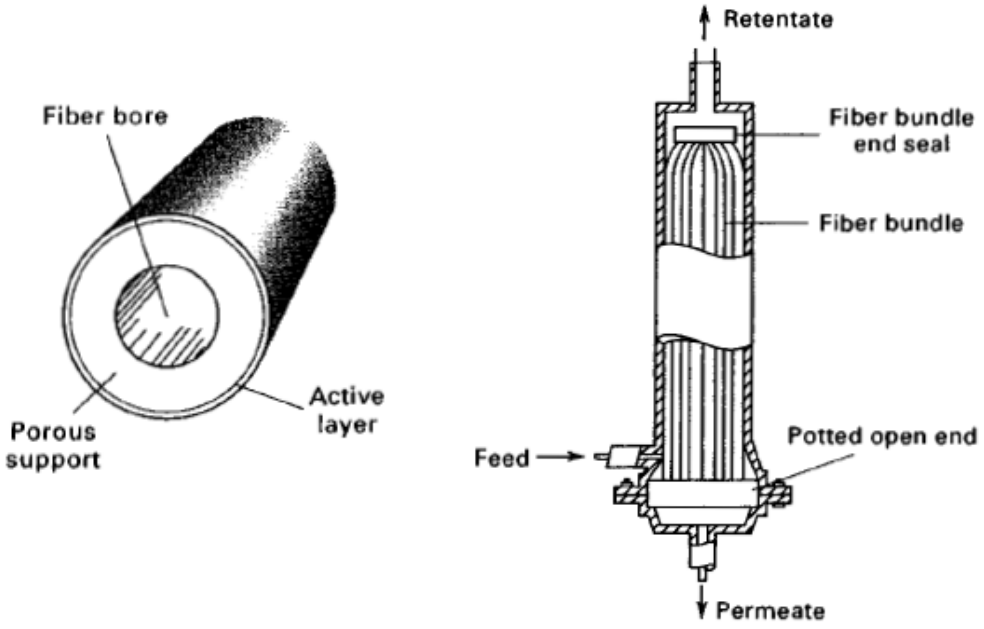


(a) (b)

Figure 2.6 - Flat sheet assembled into commercial modules: (a) plate and frame and (b) membrane cartridge (Seader & Henley, 1997) (United States Environmental Protection Agency, 2005)

Tubular geometries are usually achieved by arranging the membranes into one of two modules: hollow fibres or spiral wounds. Hollow fibres modules are comprised of long and very narrow membranes with the same denomination, typically bundled together longitudinally and encased in a pressure vessel. Commercial hollow fibre modules may have several hundred to over ten thousand fibres. Most hollow fibre systems are operated in dead-end and are periodically backwashed to remove the accumulated particles. A hollow fibre membrane and an assembled commercial module are illustrated in Figure 2.7. (United States Environmental Protection Agency, 2005)

Lastly, spiral wounds are a “sandwich arrangement” of two flat membrane sheets, separated by spacers for the flow of the feed and permeate, wrapped around a central perforated tube to assemble a module that is inserted into a pressure vessel. Permeate goes through the membrane, travelling inward in to the central collection tube, where exits the membrane through either directions. Figure 2.8 illustrates this geometry. (Seader & Henley, 1997) (United States Environmental Protection Agency, 2005)



(a) (b)

Figure 2.7 - A hollow fibre membrane (a) and a common hollow fibre module (b) (Seader & Henley, 1997)

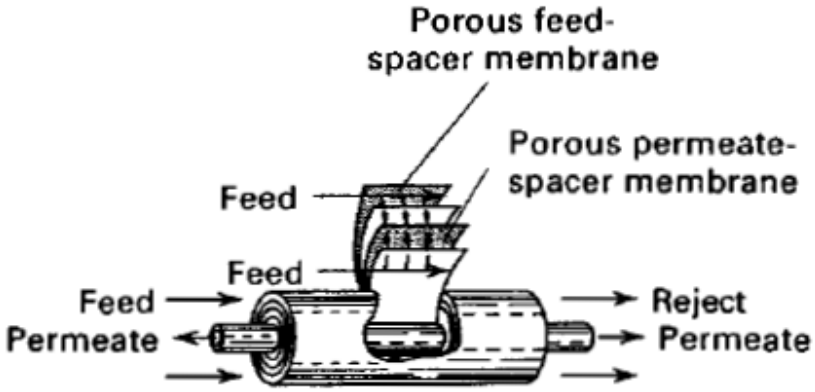


Figure 2.8 - Spiral wound membrane module (Seader & Henley, 1997)

There are several factors that can influence the choice of membrane module such as: fouling, suspended solids concentration, feed viscosity, pressure drop, maintenance, cost and ease of cleaning. (Cardew & Le, 1998) Table 2.2 summarizes some of these factors, comparing the membrane modules previously stated.

Table 2.2 - Typical characteristics of commercial membrane modules. (Seader & Henley, 1997) [1]Packing density: membrane surface area per unit volume of module; [2]D, dialysis; [3]PV, pervaporation; [4]GP, gas permeation

	Plate and Frame	Hollow Fibre	Spiral Wound
Packing density[1], m^2/m^3	30 to 500	500 to 9000	200 to 800
Resistance to fouling	Good	Poor	Moderate
Ease of cleaning	Good	Poor	Fair
Relative cost	High	Low	Low
Main applications	D[2], RO, PV[3], UF, MF	D[2], RO, GP[4], UF	D[2], RO, GP[4], UF, MF

2.1.2.4 Internal Structure

The last classification considered was membrane's internal structure. Symmetric membranes have an uniform structure in terms of density and pore structure throughout the cross-section (Figure 2.9 (a)), while asymmetric membranes are composed of two or more different layers or have a graded construction (Figure 2.9 (b)), where the pores size gradually decreases throughout the membrane. NF and RO membranes are typically asymmetric, having a multilayer structure (composite, Figure 2.9 (c)), while MF and UF membranes can be symmetric or asymmetric. (Scott & Hughes, 1996) (United States Environmental Protection Agency, 2005)

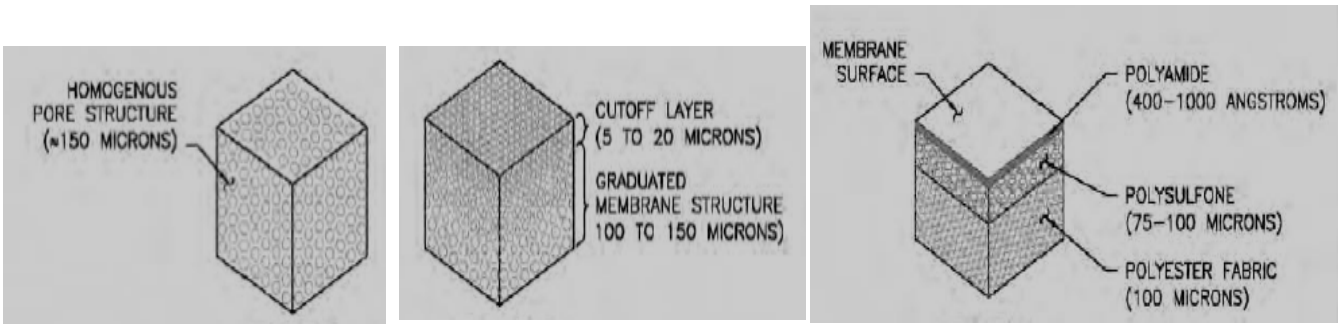


Figure 2.9 - Membrane internal structure: (a) symmetric, (b) asymmetric and (c) composite (asymmetric) (United States Environmental Protection Agency, 2005)

2.1.3 Membrane Materials

Membranes are manufactured in different materials including polymers, ceramics, metals and even glass. Not all materials are available for every membrane process, for example, reverse osmosis are almost exclusively made of polymers, whilst glass is limited to the ultrafiltration. Polymers are the main material used in membrane manufacture, followed by ceramics. The choice between both depends on the nature of the process; particle size, pH and temperature

operating range and the resistance to the chemicals and bio-organisms used are often factors to take into consideration. (Scott & Hughes, 1996)

2.1.3.1 Polymeric Membranes

As previously stated, the vast majority of industrial membranes systems uses polymeric membranes. Several polymers are used to its manufacture, such as cellulose acetate, poyamide, polysulphone, polyethersulphone, polyvinylidenedifluoride, polyacrylonitrile, or polytetrafluoroethylene. Cellulose acetate was one of the first materials to be ever used in membrane manufacture. CA is still widely used due to its hydrophilicity, manufacturing flexibility in terms of pore sizes, low cost and ease of manufacture. Figure 2.10 enumerates the general advantages and downsides of polymeric membranes. (Scott & Hughes, 1996) (Cheryan, 1998)

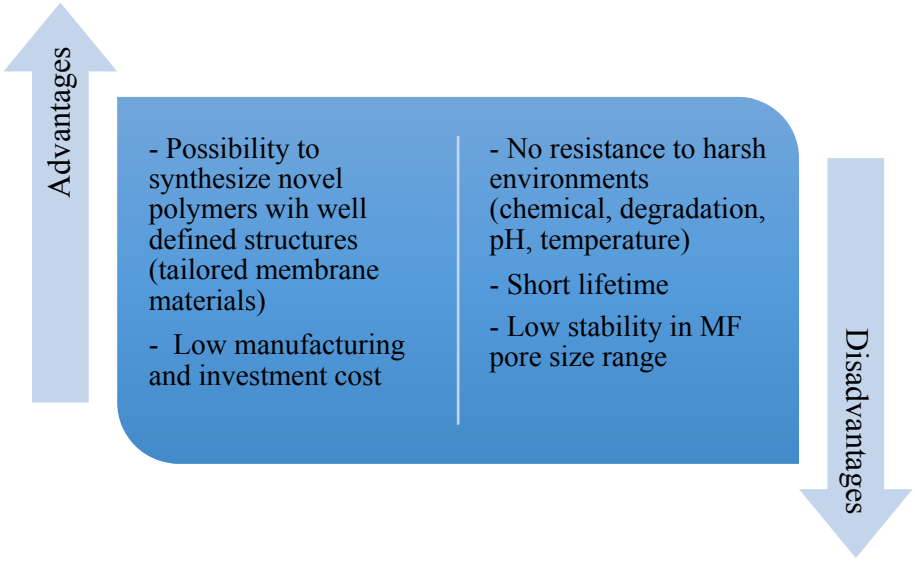


Figure 2.10 - Advantages and disadvantages of polymer based membranes (Azevedo, 2016) (Staszak, Karas, & Jaworska, 2013)

2.1.3.2 Ceramic Membranes

A ceramic membrane can be described as a fine sieve consisting of several layers of one or more different ceramic materials. Usually, the bottom layer provides mechanical support, while the top layer is responsible for the actual separation. The layers in-between bridge the pore size differences. Figure 2.11 shows a schematic representation of these layers. (Li K. , 2007)

Ceramic membranes are usually used for ultrafiltration or microfiltration and are made from aluminium, titanium or silica oxides. These membranes are chemically inert and stable at high temperatures, making them suitable for food, biotechnology and pharmaceutical applications. Furthermore, ceramic membranes are also widely used in wastewater treatment and in water

desalination. Figure 2.12 summarize the advantages and drawbacks of ceramic membranes. (Baker, 2004)

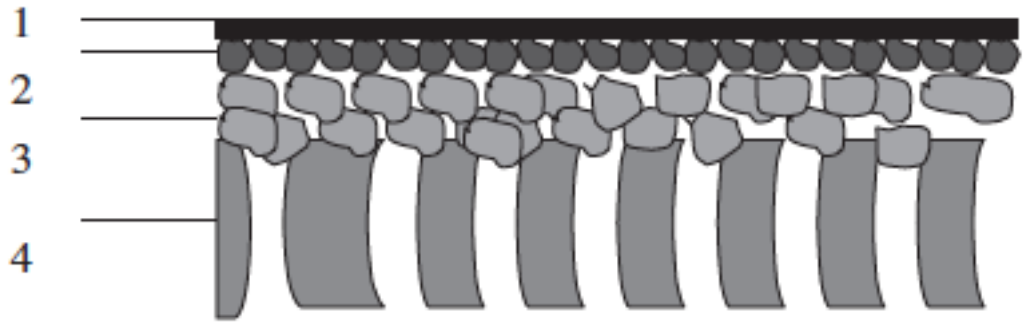


Figure 2.11 - Schematic representation of an asymmetric composite membrane; 1 – Modified separation layer (Dense or < 2 nm); 2 – Separation layer (2-50 nm); 3 – Intermediate layer(s) (50-1000 nm); 4 – Porous support (1-15 µm) [16]

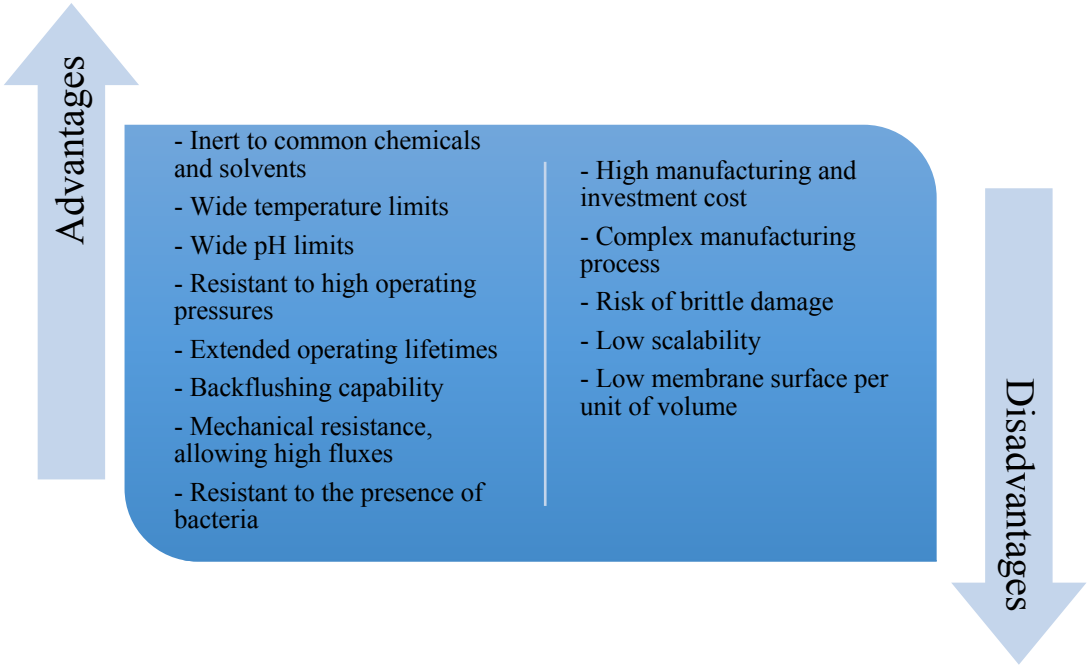


Figure 2.12 - Advantages and disadvantages of ceramic based membranes (Cheryan, 1998) (Staszak, Karas, & Jaworska, 2013) (Amin, Abdallah, Roushdy, & El-Sherbiny, 2016)

2.2 Ceramic Membranes Manufacturing Process

In general, preparation of ceramic membranes implicates several steps: (1) formulation of the particle suspension; (2) casting of the suspension into a membrane module such as a flat sheet or a hollow fibre; (3) consolidation of the membrane module by a heat treatment at high temperatures (sintering). Additionally, membranes can further go through a coating step using dip-coating, sol-gel or chemical vapour deposition (CVD) processes in order to produce a composite membrane. Slip casting, tape casting, extrusion and pressing are some of the casting

methods used in the manufacturing of ceramic membranes. Phase-inversion methods, widely used in manufacturing of asymmetric polymeric membranes, have also been recently used in ceramic membranes production. (Li K. , 2007) (Li & Kingsbury, 2008)

2.2.1 Casting Methods

2.2.1.1 Slip Casting

Slip casting is one of the most commonly used methods in membrane manufacture. In this method, a well-mixed powder suspension is poured into a porous mould and the solvent present in the suspension is extracted through the pores of the mould due to capillary force. The particles precipitate on the surface of the mould, forming the membrane layer. This consolidation must occur fast enough so that the particles do not penetrate into the mould's pores. It is a well-known, traditional method, however its casting time is usually very long. Furthermore, the membrane thickness is difficult to control, leading to thickness limitations. Slip casting method is illustrated in Figure 2.13. (Li K. , 2007)

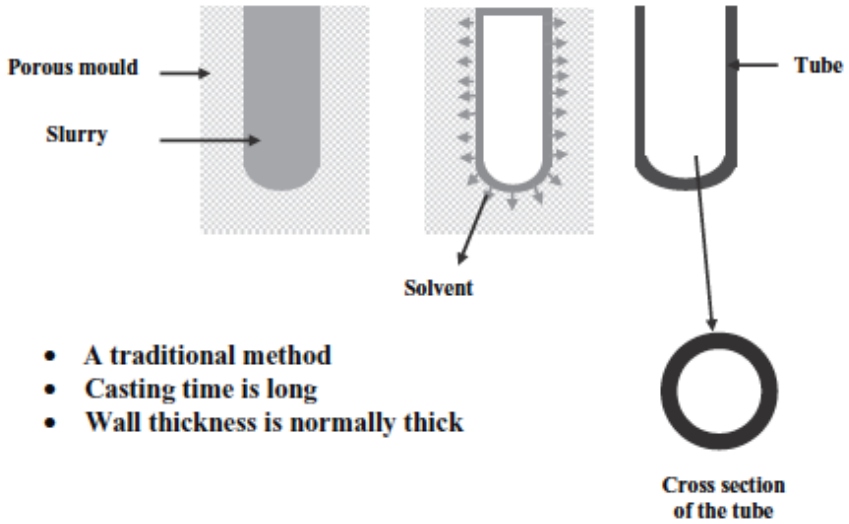


Figure 2.13 - Slip casting method (Li K. , 2007)

2.2.1.2 Tape Casting

Flat sheet ceramic membranes are often produced by tape casting. The method consists of a stationary casting knife, a powder suspension reservoir, a moving carrier and a drying zone. The casting suspension is poured into the reservoir behind the casting knife and the carrier is set in motion. The thickness of the casting layer is determined by the gap between the knife blade and the carrier. The reservoir depth, the speed of the carrier and the viscosity of the dope can also be variables to the process. The casted layer goes into a drying chamber and the solvent evaporates from the suspension, leaving the dry membrane on the carrier surface. This process can be observed in Figure 2.14. (Li K. , 2007)

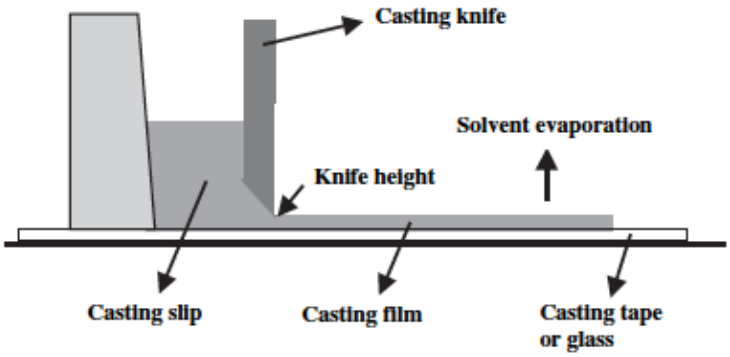


Figure 2.14 - Tape casting method (Li K. , 2007)

2.2.1.3 Pressing

Disk inorganic membranes are commonly prepared by the pressing method. As illustrated in Figure 2.15, the particle consolidation into a dense layer occurs by an applied force. This method had often been used in the manufacture of ceramic membranes permeable to oxygen or hydrogen. The disc diameter is usually a few cm, while its thickness is about 0,5 mm. (Li K. , 2007) (Biron, Santos, & Zeni, 2008)

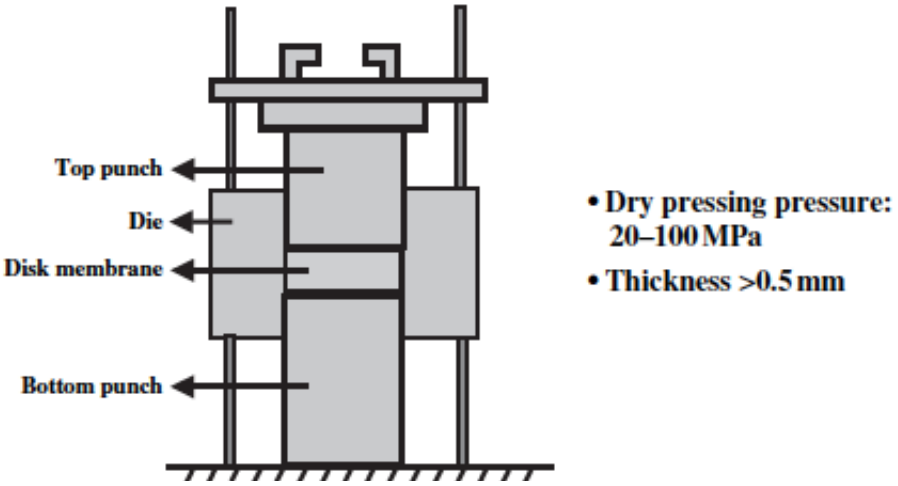


Figure 2.15 - Pressing method (Li K. , 2007)

2.2.1.4 Extrusion

Extrusion is a simple and very productive method of manufacturing ceramic membranes. It is usually applied in the production of porous ceramic tubes. In this process, a homogeneous stiff paste is compacted and shaped by forcing it through a nozzle (Figure 2.16). The die dictates the shape, porosity, and pore size distribution of the final product. Extrusion relies on plastic deformation of the slurry and evaporation of any remaining solvent to keep the membrane in its

desired shape. Extruded membranes display a homogeneous cross-sectional microstructure. (Li K. , 2007)

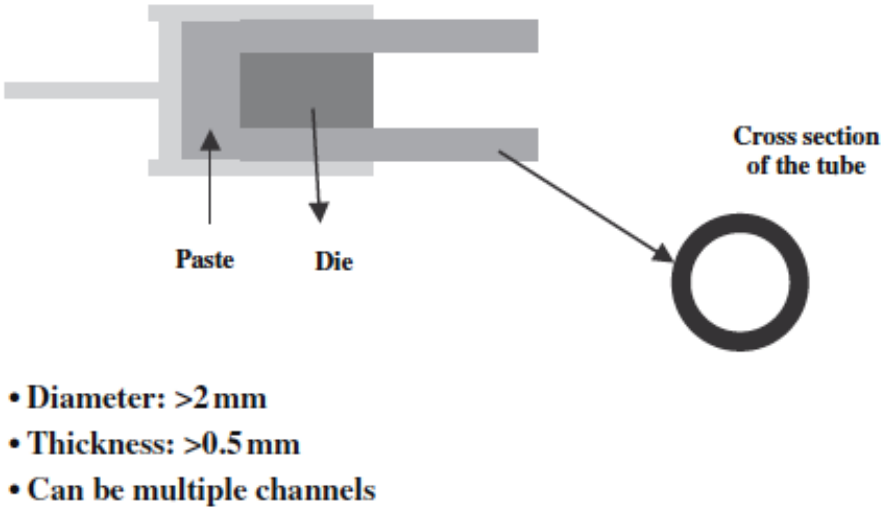


Figure 2.16 - Extrusion method (Li K. , 2007)

2.2.1.5 Phase-Inversion

The phase-inversion process is one of the most useful methods for the fabrication of polymeric membranes and has been adapted to ceramic membranes manufacturing. Phase-inversion achieves a controlled polymer transformation from a liquid phase to a solid phase. This solidification is generally preceded by a liquid-liquid demixing caused by the contact of the casting solution with a non-solvent not well miscible with the polymer but miscible with the solvent. After the demixing into a polymer-lean and a polymer-rich phase, the latter will start solidifying, composing the solid membrane matrix, while the polymer-lean phase will lead to the pores in the solidified material. (Li K. , 2007) (Holda & Vankelecom, 2015)

This technique involves preparing a homogeneous casting solution consisting of one or more polymers in a selected solvent or solvent mixture and possibly one or more non-solvents, surfactants and other additives such as inorganic salts. (Charcosset, 2012)

The phase-inversion process can be achieved via two different separation mechanisms:

- **Thermally induced phase-separation,** by cooling a casting solution that contains a latent solvent displaying only a limited ability to dissolve the polymer. (Charcosset, 2012)
- **Diffusion induced phase-separation,** by contacting a casting solution to a non-solvent vapour or liquid. Three methods have been developed to reach DIPS, which are shown in Figure 2.17:
    - **Immersion precipitation:** when the casting solution is immersed into a non-solvent bath, the non-solvent diffuses into the casting solution and the

solvent diffuses from the casting solution into the bath, causing a fast precipitation of the casting solution from the top surface downwards;

- **Vapour adsorption:** exposing the casting solution to a vapour containing non-solvent will cause its adsorption and consequently the precipitation of the casting solution;
- **Solvent evaporation:** the casting solution must be prepared with a volatile solvent, a less or no volatile non-solvent and a polymer. The evaporation of the volatile solvent will trigger the precipitation. (Wang, Chen, Hung, & Shammas, 2011)

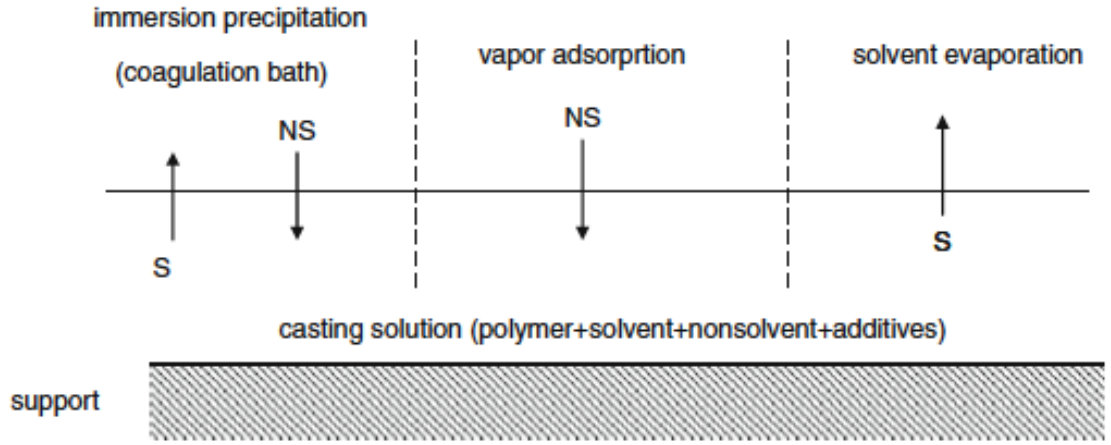


Figure 2.17 - Schematic representation of the three DIPS processes (S: solvent; NS: non-solvent) (Wang, Chen, Hung, & Shammas, 2011)

In ceramic membranes casting using phase-inversion, the ceramic/polymer/solvent system can be seen as a suspension of polymer coated ceramic particles. Once precipitation has taken place, the ceramic particles become immobilized. (Li & Kingsbury, 2008)

During phase-inversion, two-layered membranes are synthetize: a thick layer containing finger-like pores over a thin layer free of large pores. The finger-like pores formation can be described by a phenomenon called viscous fingering that occurs when two fluids with different viscosities come into contact. Due to high concentration of non-solvent at the interface, polymer precipitation leads to a steep increase in the viscosity of the suspension in this area, causing non-solvent inflow through the suspension to result in finger-like void growth. Since there is less non-solvent within the suspension than at its interface, the precipitation rate is lower within the suspension and, consequently, the finger-like void growth proceed until it reaches a critical suspension viscosity. (Ren, Fang, Gu, Winnubst, & Chen, 2014) (Ranieri, Mazzei, Wu, Li, & Giorno, 2016)

The choice of polymer, solvent and non-solvent are crucial to the morphology of the membrane casted. For example, if the non-solvent has a high miscibility with the solvent, demixing between phases happens instantaneously and a finger-like morphology is achieved. However, if

the non-solvent has low miscibility with the solvent, demixing is delayed, precipitation is slow and sponge-like morphology is obtained. (Guillen, Pan, Li, & Hoek, 2011)

3

MANUFACTURING PROCESS

The ceramic membranes manufactured by Smart Separations go through four different stages, as orderly shown in Figure 3.1. In this work, a larger focus will be given to the optimisation of the casting process.

Figure 3.1 - Manufacturing steps of Smart Separations' membranes (Azevedo, 2016)

3.1 Dope mixture

Smart Separations' manufacturing process starts by mixing α-alumina, the ceramic support material of the membranes, with an organic solvent, a polymer and a dispersant. Firstly, the dispersant and the alumina are milled in the solvent inside a rotary mixer until an homogeneous solution is obtained. Then, after a certain amount of time, the polymer is added to the process. After a standard mixing time to achieve homogeneousness, the suspension is degassed in a vacuum chamber to remove all the air bubbles inside, prior to casting.

3.2 Casting

After degassing, the suspension is ready to be casted. In the past, Smart Separation's casting was similar to tape casting described in section 2.2.1.2, combined with phase-inversion. However, the dope mixture was improved, which led to a need of changing the casting process. Prior to this study, casting was performed by filling a plastic casting mould (Figure 3.2) with dope and manually dipping it in a recipient full of water (non-solvent). The dope is then left underneath the water for a period of time (the amount required to phase-inversion occur) at ambient temperature. After casting, the ceramic "green" body is detached from the mould and dried to remove the water in excess, prior to sintering.

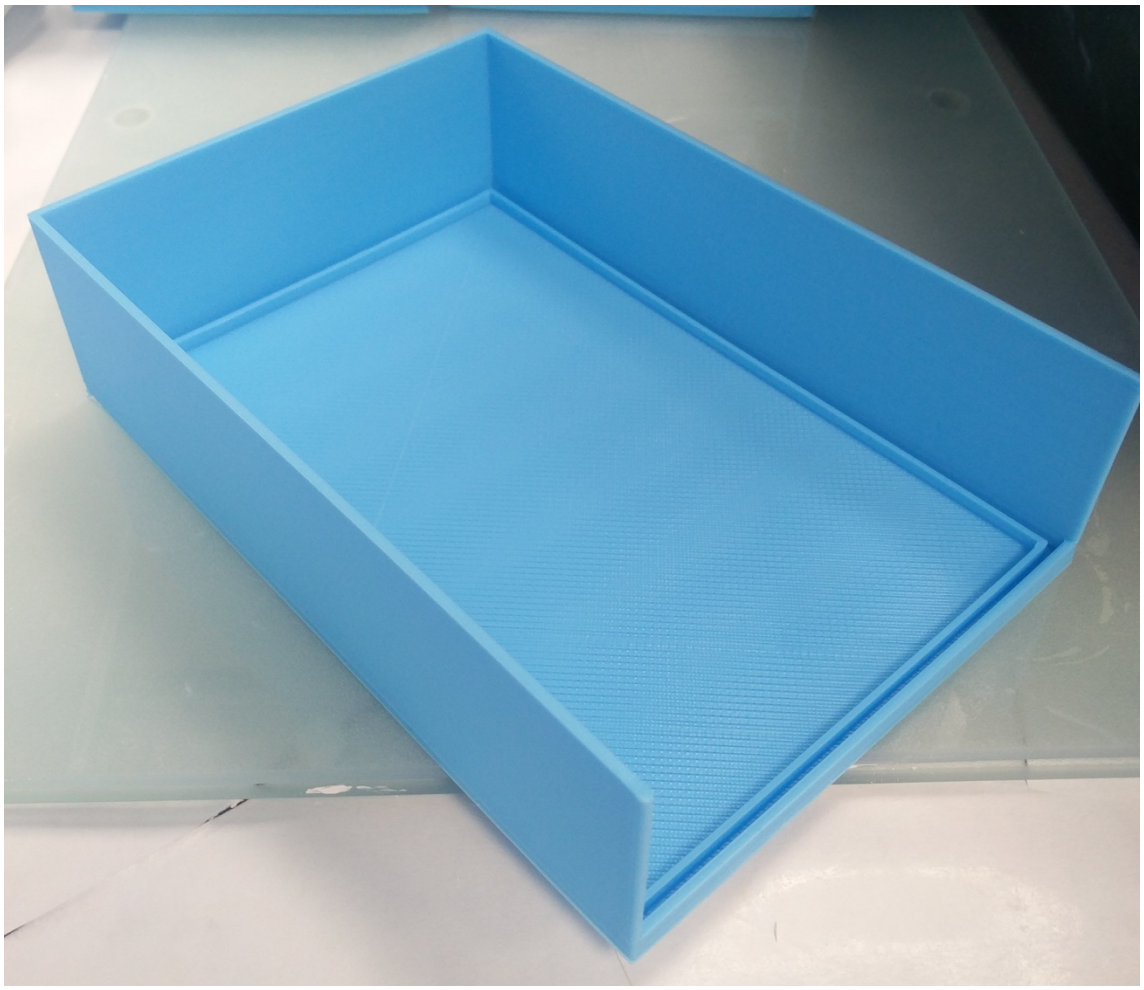


Figure 3.2 - Membrane casting mould (dimensions: 10 x 20 cm)

3.3 Sintering

The heat treatment has two main stages: the burnout and the sintering. The polymer, working as the pore-former, has already completed its goal and its presence in the final membrane compromises the consistency of the ceramic membrane. Hence, on the first stage the burning of the polymer occurs at a temperature below 1000°C. Afterwards, the temperature is increased to the sintering temperature of alumina to eliminate any remaining binder or solvent and most importantly to interconnect the particles contained in the dope in order to consolidate the membrane ceramic structure through sintering. Fusion of the alumina micro particles is done by approaching its melting point, decreasing its porosity, while changing grain size and shape and changing pore size and shape during sintering, becoming a lot more resistant afterwards. (Azevedo, 2016)

3.4 Lapping

After sintering, both top and bottom surface have their pores closed. To open these at a determined pore size, lapping is required. The removal of these surfaces is highly controlled, allowing tight control and accuracy of the pores size. Lapping allows the reduction of the batch-to-batch variability, while reducing manufacturing errors. Lapping is a final abrasive finishing operation that can correct minor shape defects, refines surface finish and produces close fit between mating surfaces (dimensional flatness). (Azevedo, 2016)

4

MATERIALS AND METHODS

In this chapter, materials and equipment used during dope mixing characterisation, membrane casting and membrane characterisation processes are described. The methods used for membrane casting are also explained.

4.1 Materials

4.1.1 Equipment for dope mixing and characterisation

4.1.1.1 Rotary mixer

A rotary mixer was tailor-made to fulfil SSL process necessities. A rotor allows the revolving movement of up to 6 recipients at once, hold together by metal parts, as Figure 4.1 shows. This movement is essential to mix and crush alumina particles inside the solution, using several ceramic balls in each batch.

Figure 4.1 - Rotary mixer and its parts

4.1.1.2 Vacuum chamber

Prior to membrane casting, the dope has to be degassed in order to become free of any air bubbles that can compromise the correct formation of the inner structure of the membranes throughout the casting process. The vacuum chamber has a stirrer attached to a rotor to facilitate the degassing process.

4.1.1.3 Viscometer

In order to characterise the dope used in membrane casting, viscosity tests are run before and after degassing. The viscometer used is a DV2T model, manufactured by Brookfield (Figure 4.2). It is directly connected with the computer so that the step program can be set accordingly to the necessities and the results can be displayed and easily saved. It displays dope's viscosity, temperature, shear rate and torque.

Figure 4.2 - Viscometer used in dope characterisation

4.1.2 Equipment for membrane casting

4.1.2.1 3D printer

As shown in the previous chapter, plastic moulds are used as container for the dope, during membrane casting (Figure 3.2). These moulds are printed in a Robox Dual extrusion 3D printer. (Figure 4.3). Material L, Material A or Material H are some of the materials that can be used as extrusion filament to create a variety of moulds.

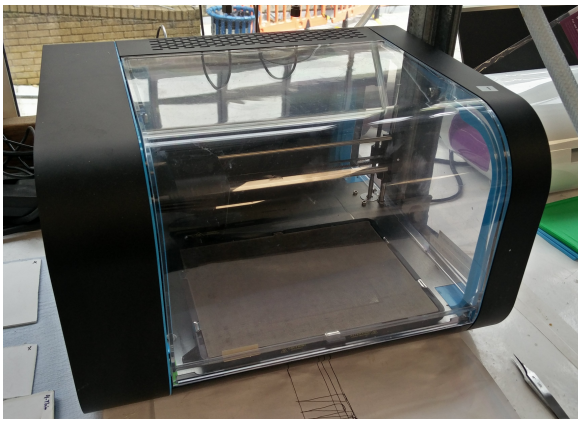


Figure 4.3 - 3D Printer used in mould manufacture (Robox Dual)

4.1.2.2 Digital scale

A digital scale is used to weigh dope that is filled in the moulds, crucial to reduce the variability batch-to-batch between membranes. The APTP-452 scale (Figure 4.4) has a maximum capacity of 3000 g and an accuracy of ± 0,01 g.

Figure 4.4 - Digital scale APTP-452

4.1.2.3 Dipping apparatus

The dipping apparatus was designed while developing this thesis. There are three main parts: the acrylic platform, especially design to fit this purpose, the step motor which provides the torque to elevate and lower the platform, and the metallic structure which holds and connects the motor to the platform.

4.1.2.4 Dehydrator

After membrane casting and prior to sintering, membranes must be dried to remove the excess of water content due to casting in submersion. To achieve that, a commercial dehydrator (usually applied in food industry) is used. The Excalibur Dehydrator shown in Figure 4.5 has a 26 hour timer and an adjustable thermostat that ranges from 40 to 75 degree Celsius.

Figure 4.5 - Excalibur dehydrator

4.1.3 Equipment for membrane characterisation

4.1.3.1 Optical microscope

An optical microscope, manufactured by AmScope, is used to observe membrane samples after casting and drying stages (Figure 4.6). A camera is attached to this equipment eyepiece, allowing to observe the images directly on the computer and save them. The software used is the AmScope v3.7, distributed by the original manufacturer.

Figure 4.6 – Optical microscope with a camera attached, connected to a computer

4.1.3.2 Digital micrometer

A digital micrometer is used to measure membrane's thicknesses after casting and drying (Figure 4.7). The equipment has a spherical top with a diameter of 6 mm. Its range is 0-25 mm and has an accuracy of ± 0,001 mm.

Figure 4.7 - Micrometer used in membrane's thickness measurement

4.2 Methodology and Methods

The manufacturing process of Smart Separations was described in Chapter 3. As stated before, this thesis focused on the casting stage with the objective of implementing a process capable of manufacturing flat microfiltration ceramic membranes without any patterns or other defects., and with good microstructure. In order to achieve this objective, the work methodology adopted throughout this thesis was adapted to fit each of the working stages shown in Figure 4.8.

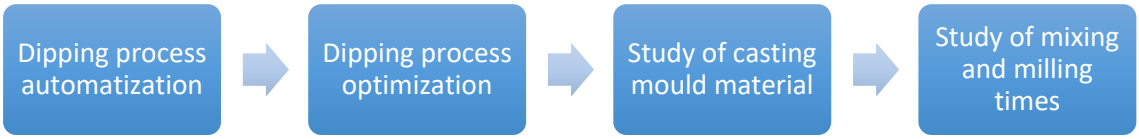


Figure 4.8 - Work methodology applied

4.2.1 Dipping process automation

During dipping process automation the methodology used was pretty straightforward: all the resources available were taken into account and a simple, functional and easy to use solution was proposed. The dipping apparatus was an adaptation of an old apparatus with a tailor-made platform designed by our team.

4.2.2 Dipping process optimization

After the process automation, the optimization of the process was based on trial and error. At this stage, the dipping velocity, the moulds used and different methods to protect the dope's top surface during submersion were the variables being tested. Many possible solutions were tried until a result led to the conclusion that the study of the casting mould material was imperative. So far, no analytical methods were employed other than visual observation, since the issue that was being studied was easy to be visually identify.

4.2.3 Study of casting mould material

During the study of casting mould material, membranes were casted using different materials (but the same design) and then they were characterized in terms of bending, flatness, existence of wavy patterns and microstructure. The membranes were compared between them to conclude which material casted the best membrane. The standard operating procedure for membrane casting was applied, to ensure that every membrane were cast equally. This *SOP* is described in the Section 4.2.5.2. The volume of dope used to fill the moulds was adjusted to provide the same dope's thickness to all the moulds.

Regarding bending, a visual comparison (using photos) was made, setting a qualitative ranking between membranes. The same analysis method was applied to the existence of wavy patterns.

In terms of flatness, the micrometer was used to measure the thickness of 8 different areas of the membrane, as shown in Figure 4.9. The average and standard deviation of each membrane allows the comparison of flatness between the casted membranes.

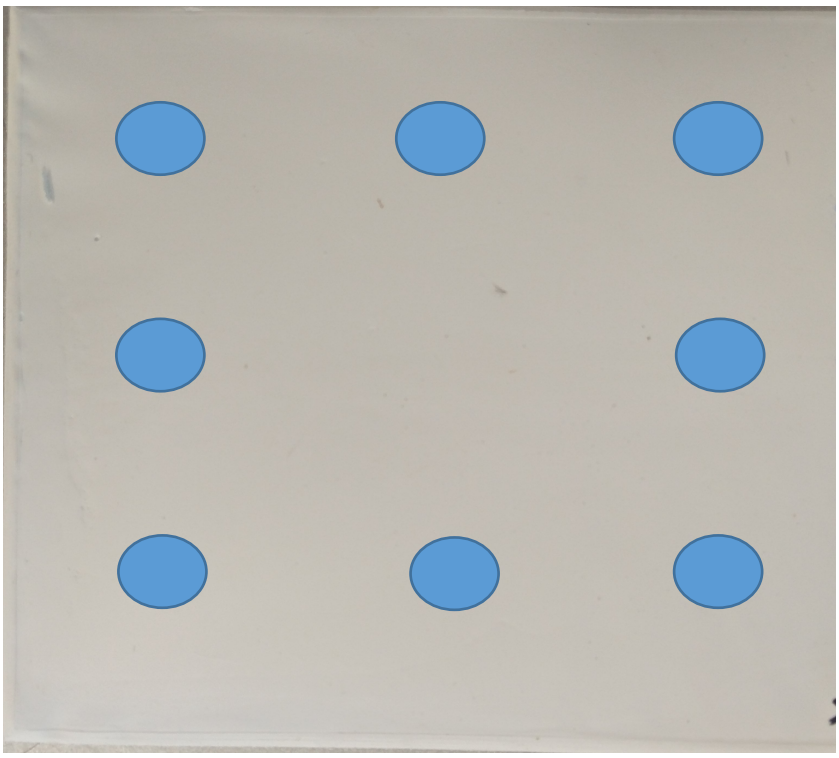


Figure 4.9 - Different areas measured to compare the flatness between membranes

Lastly, the microstructure of the casted membranes was also compared, using images retrieved from the optical microscope.

4.2.4 Study of milling and mixing times

The study of milling and mixing times focused on observing the impact of different combinations of suspension preparation times in membrane casting. The objective was to find out if it was possible to observe differences in the membrane's flatness or microstructures by changing these suspension preparation times. The flatness were measured as described in the section before. The microstructure was also visually compared, using optical microscope images. The mixing and milling times combinations are presented in Table 4.1.

Table 4.1 - Suspension preparation times combinations

Dope	Milling time (h)	Mixing time (h)
1	24	24
2	24	48
3	48	48
4	24	96
5	96	24
6	96	96

All the membranes were prepared and casted following the *SOPs* for suspension preparation and for membranes casting, presented in section 4.2.5.1 and section 4.2.5.2, respectively. All the membranes were casted in Material A casting moulds.

4.2.5 Standard operating procedures

4.2.5.1 *SOP* for suspension preparation

The standard operating procedure for suspension preparation is described below:

1 – Dissolve the dispersant in solvent.

2 – Add alumina powder to the mixture.

3 – Mill the suspension for 24 hours inside the rotary mixer.

4 – Add and mix the polymer for 24 hours.

5 – Degas the suspension.

4.2.5.2 Proposed *SOP* for membrane casting

The standard operating procedure employed for the casting of SSL's membranes is described below:

1 – Prepare the dope according to Smart Separations' *Suspension Preparation SOP*.

2 – Fill the water tank.

3 – Prepare the dipping apparatus: switch on the step motor, rise the dipping platform, remove the excess of water from the platform and set the casting mould using adhesive tape.

4 – Ensure that the platform is flat, using a spirit level.

5 – Calculate the volume necessary to fill (up to its maximum) the chosen casting mould.

6 – Measure the required volume of dope using a volumetric flask.

7 – Fill the casting mould with the dope.

8 – Ensure that the dope is evenly distributed along the mould.

9 – Lower the dipping platform.

10 – Leave the membrane submerged in water for, at least, 24 hours.

11 – Remove the mould from the water tank and carefully detach the membrane from the mould. If needed, use a spatula.

12 – Remove the excess of water on the membrane and put it to dry in the dehydrator for, at least, 12 hours.

This SOP was developed during the dipping process automation and optimization (described in Section 5.1.1) and fully applied throughout the casting mould's material tests (described in Section 5.1.3).

5

RESULTS AND DISCUSSION

5.1 Membrane casting

5.1.1 Dipping process automation and optimization

The first step towards the improvement of this manufacturing stage, was the automation of the dipping, eliminating the variability of the dipping force/speed.

The apparatus illustrated on chapter 4.1.2.3 allowed to make the dipping stage a steady and repeatable process. Moreover, it allowed to dip the casting mould in a perfectly vertical way, which is crucial to achieve a flat, even membrane, since the phase-inversion starts as soon as the water touches the dope, immediately solidifying its top layer.

On the first experiments, the dipping speed was maintained considerably low, in order to keep the water disturbance low (the container causes water agitation while entering the mass of water). This first approach resulted in uneven membranes (regarding its thickness), containing wavy patterns, as shown in Figure 5.1.

Figure 5.1 - Membrane casted at low dipping speed, showing several defects (dimensions: 9,8 x 19,6 cm)

In a first analysis, the formation of the wavy patterns was thought to be caused by the water propagation on top of the dope's surface, when it comes into contact with it. Therefore,

experiments using different permeable materials on top of the casting mould were conducted, but the results were unsatisfactory. One of the problems faced was that the air present between the dope's top surface and the layer of permeable material used remained trapped due to the water pressure, after the dipping, preventing the water from coming into contact with the dope. While trying to solve this problem, the permeable material was put into contact with the dope's surface (filling the casting mould up to its maximum), however this approach did not improve the outcome. Some of the dope remained attached to this material during its shrinkage, thus the mass transfer described in Figure 2.17 was not being well performed, compromising the microstructure formation.

Other approach, was the use of water-soluble sheets on top of the dope's surface, however these interacted with the dope, creating an undesirable paper-like layer on top of the membrane, which could have impact on its performance.

Spraying the dope's top surface with water was another method tested. The objective was to start the phase-inversion only at the surface before dipping the dope, making it more resistant to the water's flow. However, it created a pattern on the membrane's surface (as shown in Figure 5.2) due to the water droplets, and the idea was also rejected.

Figure 5.2 - Pattern caused on membrane's top surface due to water dropplets

Until this point the dipping speed was maintained considerably low, in order to keep the water turbulence low. When the dipping speed was significantly increased (up to 2,7 cm/sec), it was noticed that the membrane's top surface could remain intact if the submersion continued deeper, rather than just a few millimetres needed for wetting the dope's top layer.

These studies helped to further understand the appearance of wavy patterns. Even though a perfectly smooth surface was achieved right after the dipping, moments later (just a few seconds) the wavy pattern previously described was observed. This pattern had no relation to the effect of the water propagation during the dipping, but rather it was caused due to the shrinkage of the membrane.

This phenomenon was clearly observed in some moulds that had some of its walls bent. These defected walls allowed the dope to attach more easily than to the straight walls. The membrane area next to the straight walls showed a wavy pattern, created after the detachment from the walls, while the area next to the bent walls were perfectly flat.

This result led to the conclusion that the shrinkage was also responsible for the unwanted patterns. In order to achieve a perfectly flat membrane, this effect had to be minimized, using the right design and material to keep the membrane attached to the sides.

The first satisfactory result was obtained using Material P, creating a perfectly flat membrane. The fact the dope has good adhesion to this material and that the walls are really thin (bending while the membrane shrinks, as shown in Figure 5.3) are the likely two main reasons for the achievement of a good result.

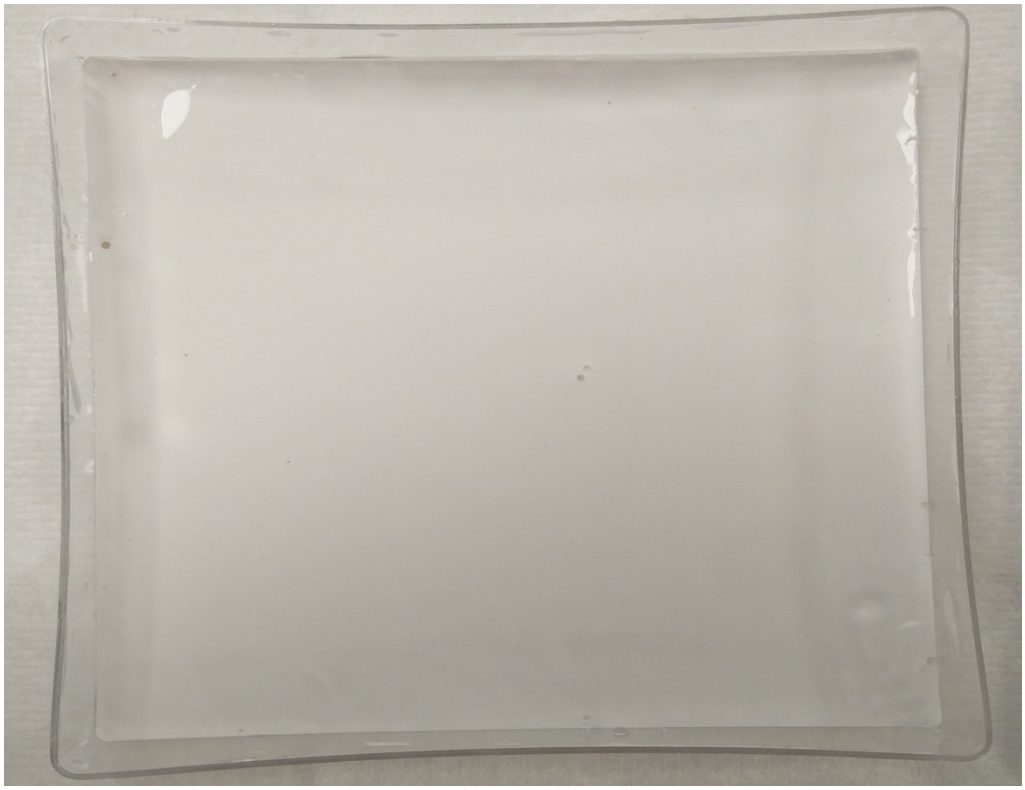


Figure 5.3 - Membrane casted in Material P (dimensions: 10 x 10 cm)

Despite this apparent satisfactory outcome, the membranes casted in Material P revealed several issues. First, it was really difficult to perfectly detach the casted membrane from the mould, eventually breaking the membranes in many parts. Besides that, the microstructure obtained on this membranes presented several defects as shown in Figure 5.4.

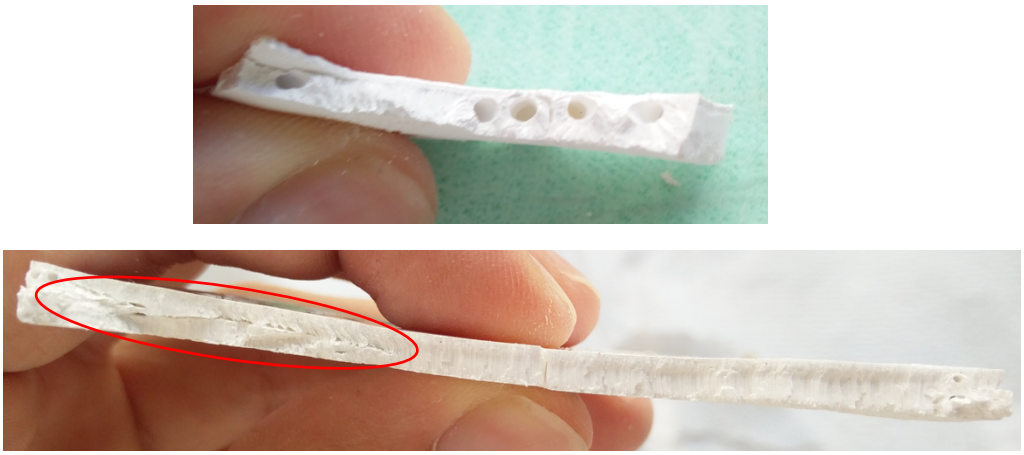


Figure 5.4 – Membranes casted on Material P containing microstructural defects (Top: voids inside the membrane; Bottom: multi-layered membrane)

Since it was supposed that the high adherence between the dope and the Material P was the cause for these issues, several tests were conducted using adhesive vinyl paper on different areas of the mould. However, the paper's glue was not strong enough to withstand the infiltration of water, curling the vinyl paper, and affecting the casted membranes (Figure 5.5). Material P was then discarded as a solution, since it only could solve the flatness problem while compromising the microstructure.

Figure 5.5 - Membrane casted on Material P coated in vinyl paper (dimensions: 10,5 x 10,5 cm)

5.1.2 Casting mould design

During these studies it was also evident that the casting mould's design could be redefined. Since the water flow was no longer a problem, the walls of the original design (which were there to prevent the water coming from the sides) could be eliminated and the design became simpler, easier and cheaper to 3D-print. The original design used and the improved one can be observed in Figure 5.6.

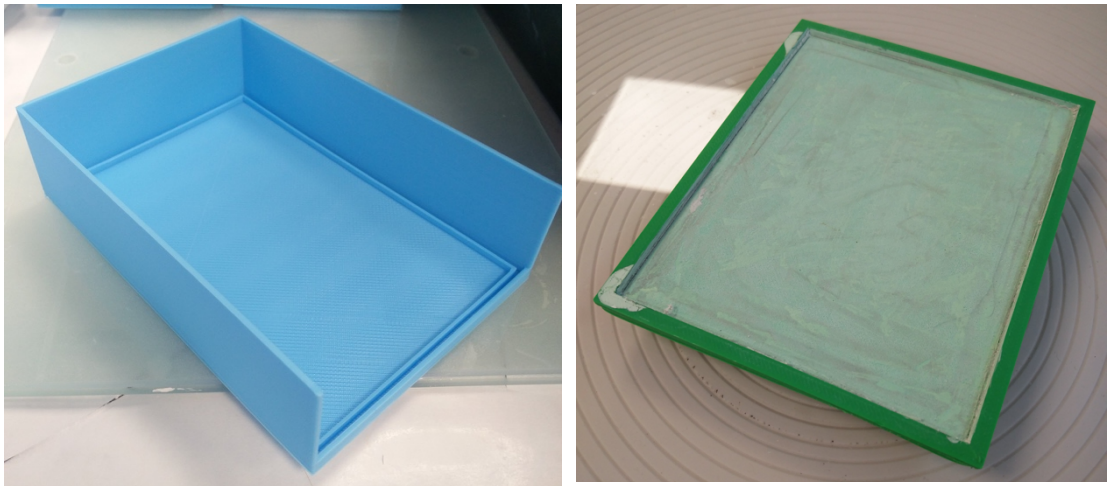


Figure 5.6 - Left: Original mould design used in membrane casting (dimensions: 10 x 20 cm); Right: Improved design in this project (dimensions: 10 x 12 cm).

5.1.3 Study of casting mould material

The results achieved up to this point, led to the conclusion that studies on the material used to cast the membranes should be performed. To achieve the goal of flat, pattern-free membranes, different casting moulds materials have been used. The materials used were the ones available at Smart Separations: Material A, Material L, Material T, Material H and Material R moulds were 3D-printed, while Material M and Material U moulds were made by our designer. The membranes casted were characterized in terms of bending, flatness, existence of wavy patterns and microstructure.

5.1.3.1 Bending

In terms of bending, only the Material A and Material T casting mould materials were considered satisfactory. The use of Material M, Material U and Material R casting moulds resulted in extremely bent membranes. The Material L and Material H casting moulds did not have such poorly outcome, however it was still considered unsatisfactory. The bending present in the membranes is due the poor adhesion between the dope and the material. The figures below illustrate this issue, with the membranes still on their mould, before the drying stage.

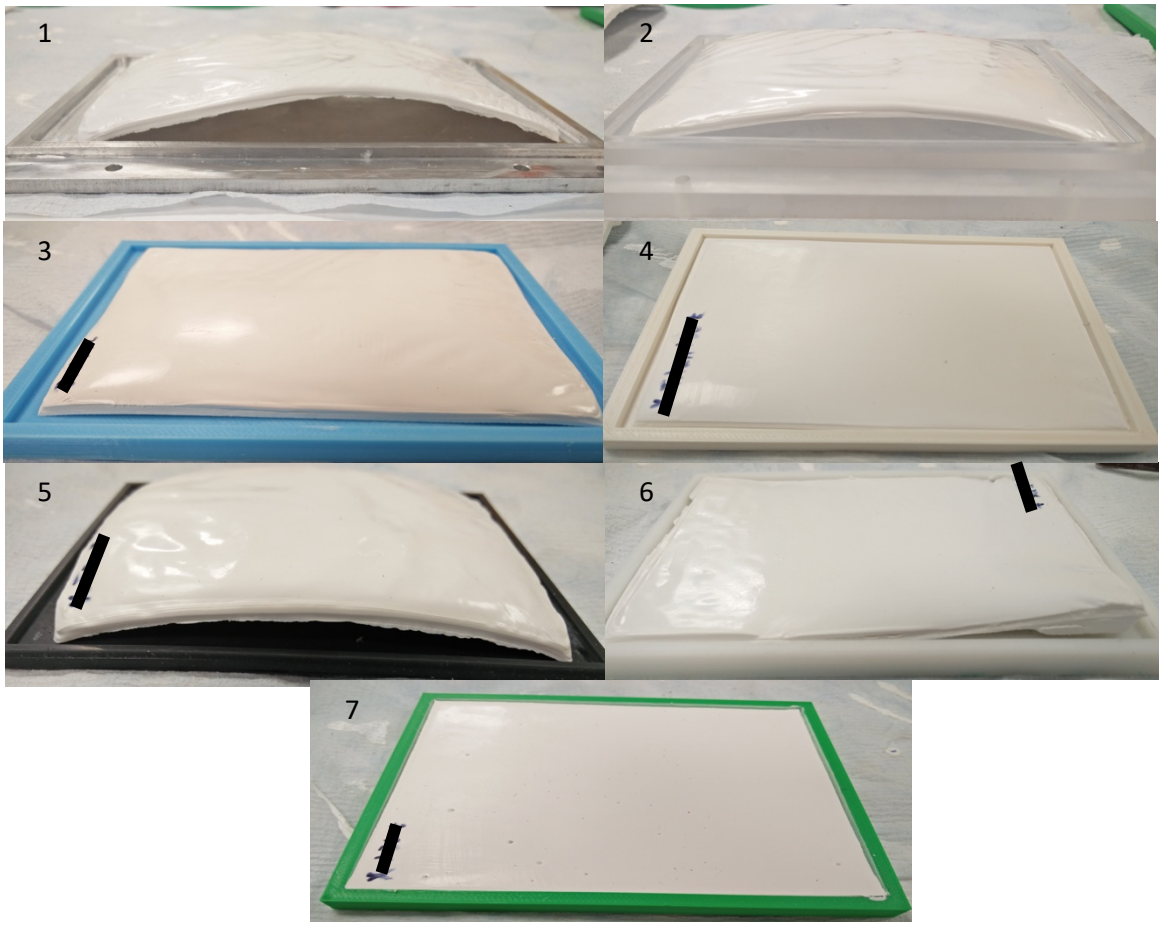
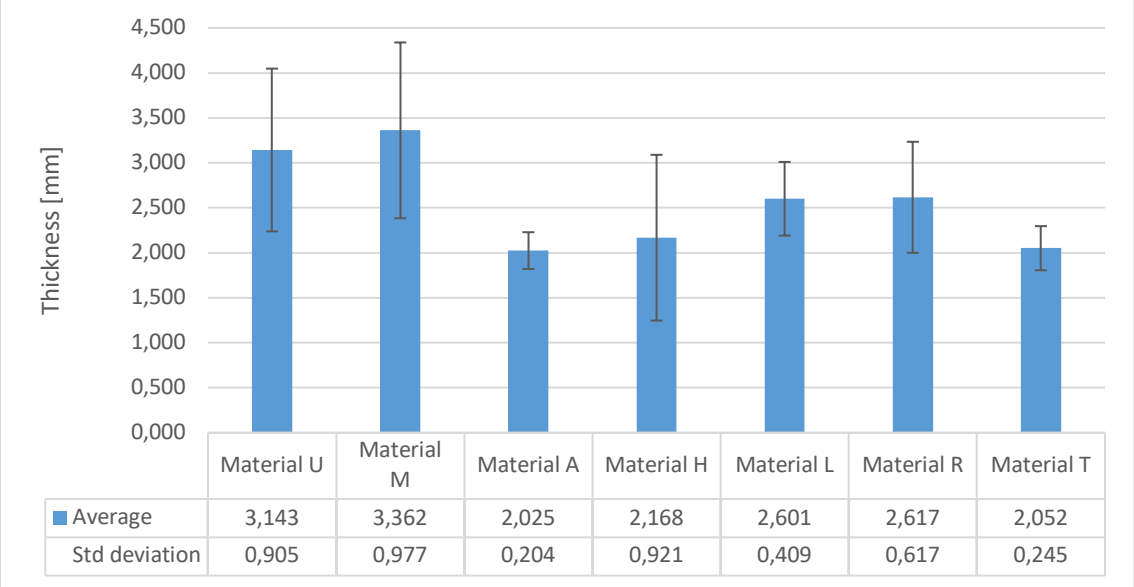


Figure 5.7 – Bending test results (1- Material U; 2 – Material M; 3 – Material L; 4 - Material T; 5 - Material R; 6 – Material H; 7 – Material A); Dimensions: 9,5 x 16 cm (1 and 2), 10 x 12 cm (3, 4, 5, 6 and 7)

5.1.3.2 Flatness

The flatness was quantitatively characterized by measuring 8 different points of the thickness of the casted membrane. The results are shown in Figure 5.8.The values measured can also be consulted in Appendix A.



	Material U	Material M	Material A	Material H	Material L	Material R	Material T
Average	3,143	3,362	2,025	2,168	2,601	2,617	2,052
Std deviation	0,905	0,977	0,204	0,921	0,409	0,617	0,245

Figure 5.8 - Membrane thickness - average and standard deviation

The lowest standard deviations are observed in the Material A casting material, which means a more uniform membrane, and, therefore, flatter. The Material T material also achieves a very satisfactory outcome.

It is important to refer that all the membranes were casted with the same level of dope (height inside the mould, equal to 2,5 mm), therefore if the moulds were made out of the same material, the final thickness of the membrane would be similar. This is indeed true for Material A and Material T. For the others, it is possible to observe that the shrinkage happens differently.

The thickness of the membranes can also indicate the state of their microstructure. The membranes casted in the Material U and Material M moulds presented different layers due to the water infiltration beneath the dope, during the phase-inversion. As shown in Figure 5.9, there is a spongy bottom layer, which results in a thicker membrane, compared with the membranes casted in Material A or Material T moulds.

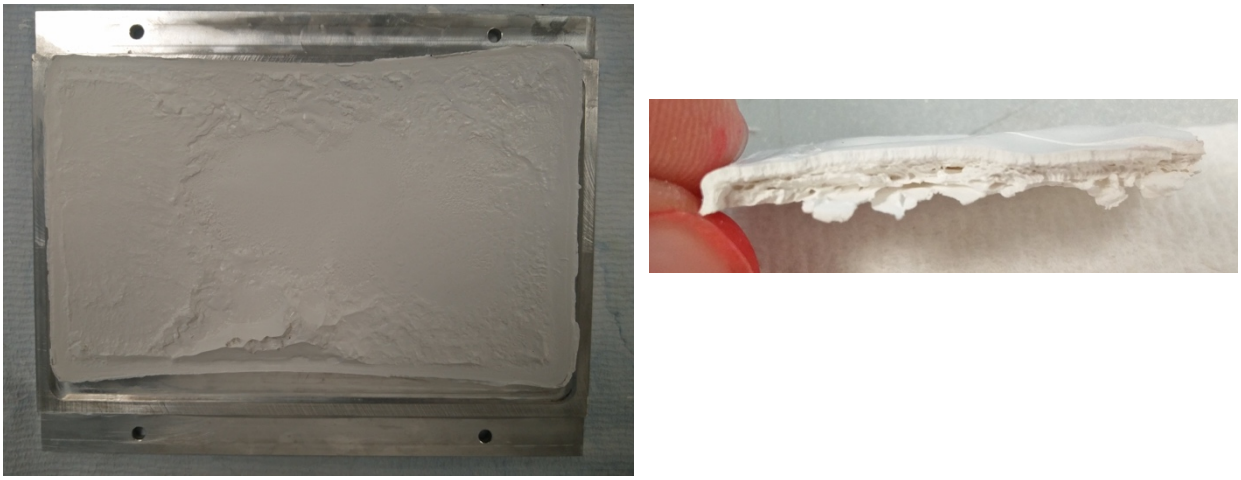


Figure 5.9 - Left: Bottom side of the membrane casted in the Material U mould (dimensions: 9,5 x 16 cm); Right: Cross section of the membrane casted in Material M mould

5.1.3.3 Existence of wavy patterns

The patterns on the top layer of the membranes are formed due to the non-uniform shrinkage of the membranes during the phase-inversion. In the casting moulds, where the dope does not attach to the material (such as the Material M, Material U, Material R and Material L casting moulds), this effect is more visible. This occurrence also leads to less flat membranes, because in the areas where there are wavy patterns, the flatness varies from point to point. Figure 5.10 illustrates this issue, with the membranes still on their mould, before the drying stage. The Material A and Material T are the only ones where this defect is not present.

Figure 5.10 – Photos of the top surfaces of the casted membranes (1- Material U; 2 – Material M; 3 - Material L; 4 - Material T; 5 - Material R; 6 – Material H; 7 – Material A); Dimensions: 9,5 x 16 cm (1 and 2), 10 x 12 cm (3, 4, 5, 6 and 7)

5.1.3.4 Microstructure

In all casted membranes it is possible to observe conical porous structures. However, depending on the casting mould used, the length, the format and the straightness of the pores varies.

The worst results were obtained on the membranes casted in Material M, Material U and Material R moulds. The pores are bent, there are multiple layers throughout the membranes and

the dimensions of the pores are also irregular. The microstructure observed in the cross sections of these membranes is illustrated in Figure 5.11.

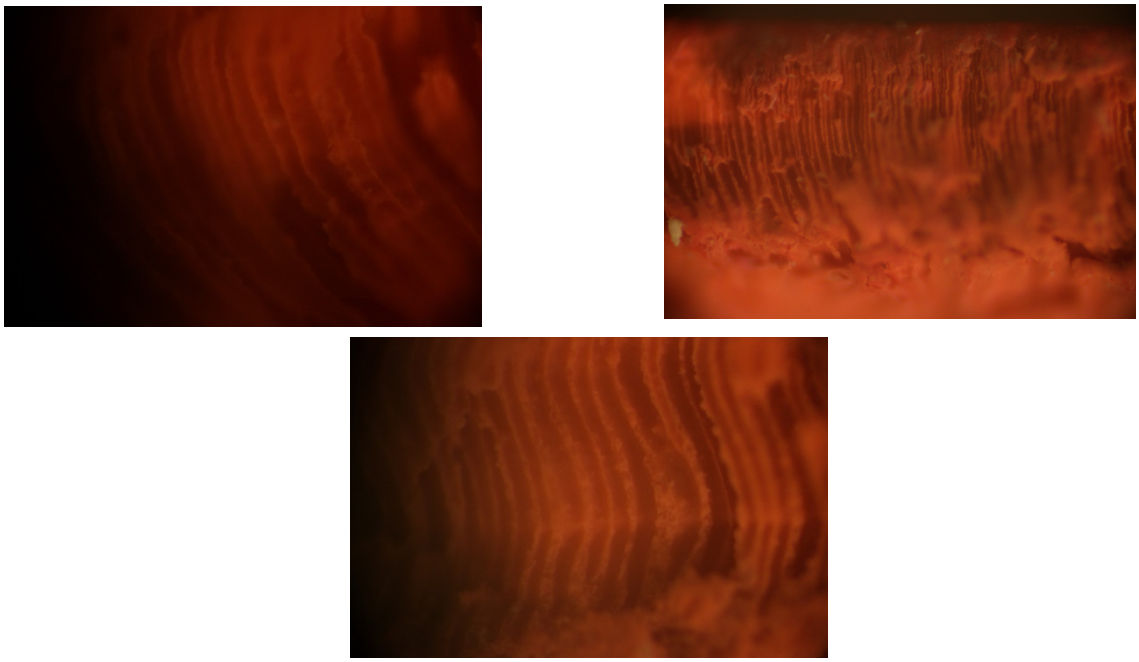


Figure 5.11 – Microscope photos (10x magnification) of casted membranes cross sections (top left: Material M mould; top right: Material U mould; bottom: Material R mould)

The membrane casted in the Material L mould showed 3 different microstructure zones, with the conical pores going through the whole thickness of the membrane. As shown in Figure 5.12, the pores seems to bend in the middle of the membrane and only a few of them reach the bottom of the membrane. Apart from that, it is also possible to observe that the pores become much wider, from the top to the bottom of the membrane.

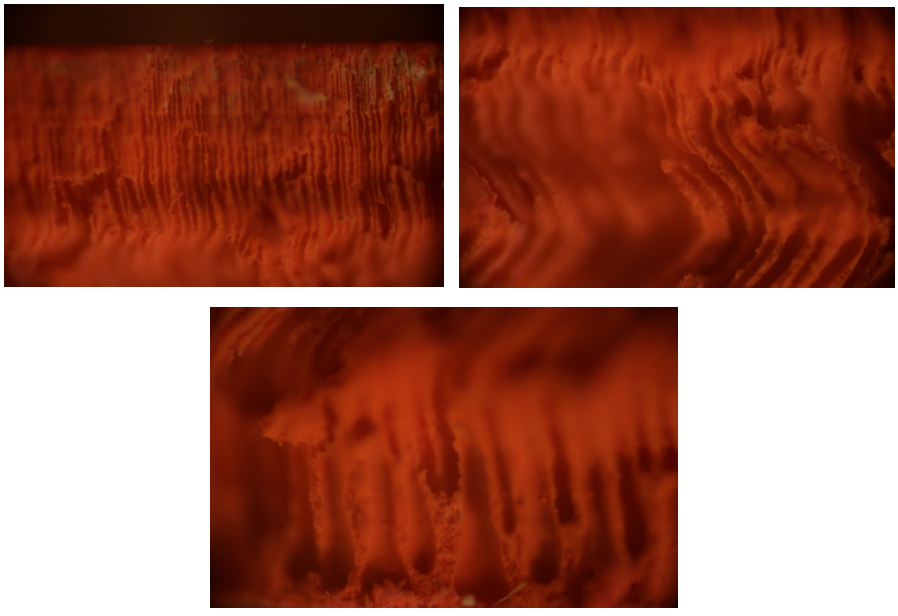


Figure 5.12 - Microscope photos (10x magnification) of the cross section of the membrane casted in Material L mould (top left: top surface; top right: middle area; bottom: bottom surface)

Finally, in the membranes casted in the Material A, Material T and Material H moulds the conical pores are well defined, as represented in Figure 5.13. Unlike the membranes observed so far, the pores visible in the cross sections of these membranes are regular and straight. They also appear to be in greater number. However, these pores only go through a portion of the thickness of the membrane. It is visible to the naked eye (Figure 5.14) that the membrane casted in Material A mould has two distinct layers. The microscope image from the bottom area of the cross section shows that this area contains no conical pores, as shown in Figure 5.15. This same result is also observed on the membranes casted on Material T and Material H moulds.

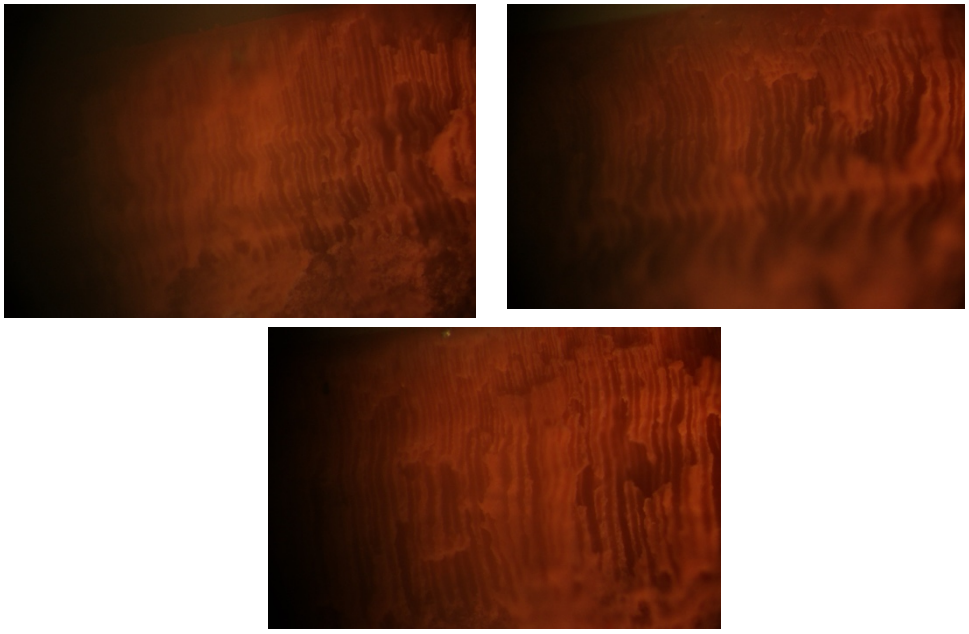


Figure 5.13 - Microscope photos (10x magnification) of the cross section of the top part of the casted membranes (top left: Material A; top right: Material T; bottom: Material H)

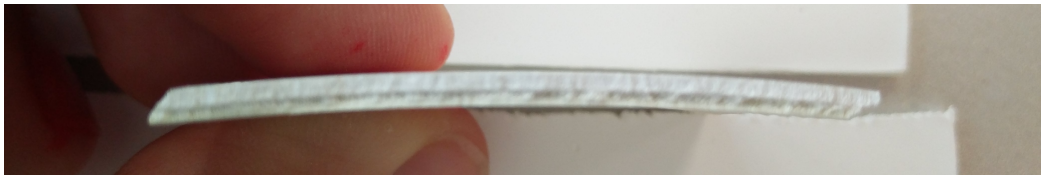


Figure 5.14 – Cross section of the membrane casted in the Material A mould

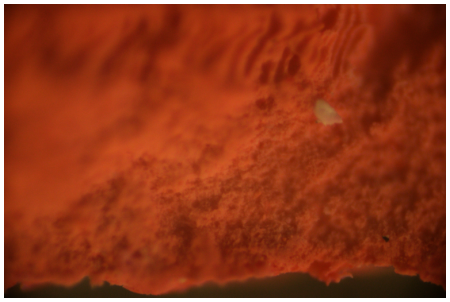
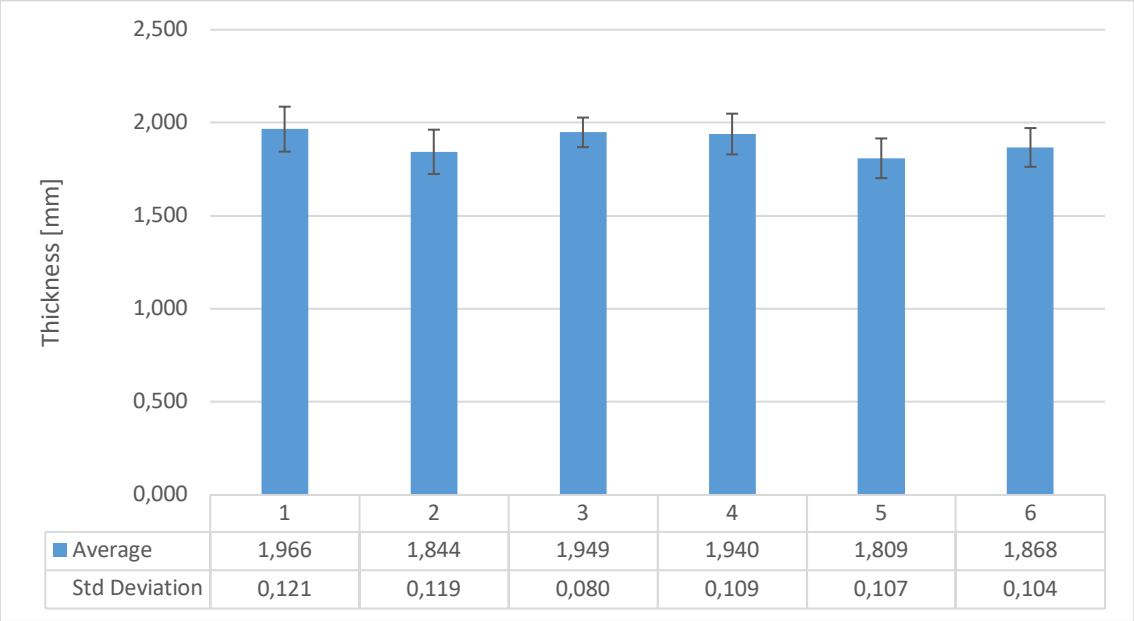


Figure 5.15 – Cross section of the bottom part of the membrane casted on the Material A mould

5.1.4 Study of mixing and milling times

The membranes casted using six suspensions with different mixing and/or milling times were analysed in terms of flatness and microstructure quality.

Regarding flatness, all the casted membranes presented similar results, as presented in Figure 5.16.



	1	2	3	4	5	6
Average	1,966	1,844	1,949	1,940	1,809	1,868
Std Deviation	0,121	0,119	0,080	0,109	0,107	0,104

Figure 5.16 - Membrane thickness - average and standard deviation

Considering the microscope images of the membranes casted using different suspension times, shown in Figure 5.17, no significant differences can be observed.

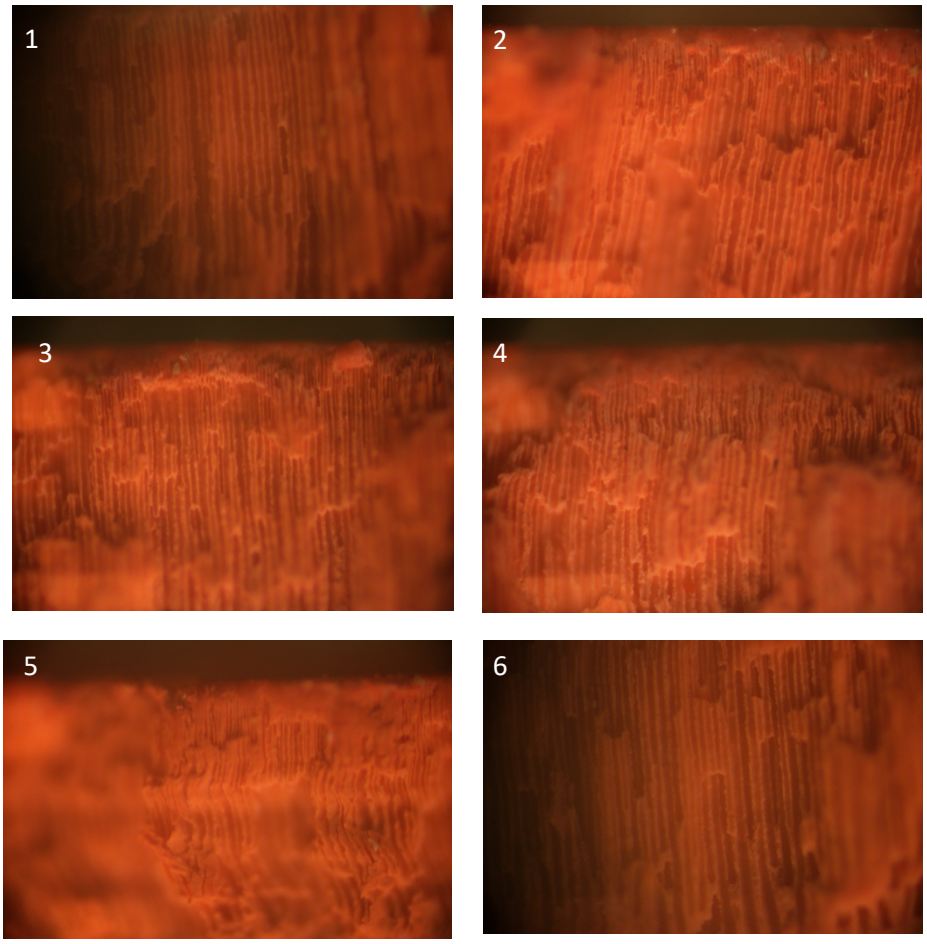


Figure 5.17 - Microscope photos (10x magnification) of the cross section of the top part of the casted membranes

6
CONCLUSIONS

With focus on the casting stage, the work developed throughout this thesis allowed to achieve a significant improvement in the manufacturing process of Smart Separations' membranes. The main objective - the manufacture of a flat, pattern-free membrane with good microstructure - was achieved after tackling the issues that were blocking this achievement (mostly, the wavy patterns and the shrinkage) with different approaches.

The automation of the dipping process was a major breakthrough to reduce the variability and improve the accuracy of this stage. Furthermore, it allowed to replicate dipping conditions, which were crucial to compare the results throughout the developed work.

The optimization of the dipping process brought important insights into the many problems faced during membrane casting. To start, it was possible to conclude that the wavy pattern was not only a consequence of water propagation on top of the dope's surface, but it was also a consequence of the green body shrinkage. At this point, it was understood that it was easier to tackle this issue by increasing the dipping velocity and controlling the shrinkage and detachment of the membrane. It was this conclusion that led to the study of different casting mould materials. The many experiments conducted during this working stage allowed establishing a *SOP* for membrane casting.

Regarding the study of the casting mould's material, Material A was the one that provided the best outcomes. In all four characteristics studied (bending, flatness, existence of wavy patterns and microstructure) this material showed a superior performance, being capable to cast the most flat and less bent membranes, with good microstructure. Material T also achieved the great results as expected, since this material is a modified Material A filament, and, therefore, it has the same behavior as Material A. The results of the casting mould's material study are summarized in Table 6.1.

Table 6.1 - Summary of the study of the casting mould's material results

	Material U	Material M	Material A	Material H	Material L	Material R	Material T
Bending	Heavily bent	Heavily bent	None	Slightly bent	Slightly bent	Heavily bent	None
Flatness (std deviation, in mm)	0,905	0,977	0,204	0,921	0,409	0,617	0,245
Existence of wavy patterns	Yes	Yes	No	Yes	Yes	Yes	No
Microstructure	Multi layered	Multi layered; bent pores	Dual layered; good conical pores	Dual layered; good conical pores	Only one layer; Bent pores	Multi layered; bent pores	Dual layer; good conical pores

As illustrated before in Figure 5.7, the membranes casted on Material M, Material U and Material R moulds were detached from it. During phase-inversion, water came into contact with the membranes from multiples directions and not only from the top surface. Therefore, the formation of the conical porous structures through the whole thickness did not occur and a spongy structure took place (example in Figure 5.9). Membrane bending might also be the reason why the microstructure on these membranes looks bent (Figure 5.11).

Although better microstructure results are achieved using Material A, Material T or Material H as casting moulds, the membrane casted on the Material L mould is the only that does not present a non-porous bottom layer. This is probably because of the interaction between the dope and the material itself. Although it is undesirable having a non-porous layer at the bottom of the membrane (the pores must be fully opened in order for the membrane to have a good performance), it can be solved with the lapping process, by removing this excess of membrane.

The study of the mixing and milling times was inconclusive. Although the results indicate that the suspension mixing and milling times have no impact in membrane casting and in the membrane itself, more studies should be done to validate this statement. The results here obtained also show the replicability and sustainability of the process, since the results obtained while using Material A moulds were all very similar.

This thesis allowed a better understanding of the behavior of dope/membrane during the casting process and provided a leap forward for the manufacturing of Smart Separations' membranes. The work developed provided the tools, the materials and the process necessary to manufacture a flat, pattern-free membrane, fulfilling most of the objectives that were proposed.

FUTURE WORK

Despite the advances made in the manufacturing process during this project, it is still possible to improve it by further studying some of the topics touched upon in this thesis. Also, several variables were neglected and their impact should be carefully study. Therefore, here it is presented a list of possible future studies:

- **Membrane performance tests:** the membranes casted throughout this thesis should be sintered, lapped and tested, in order to prove that the proposed modifications to the process improved the quality of the final product.
- **Membrane microstructure SEM analysis:** the membranes casted should be observed in a Scanning Electron Microscope for a more thorough image analysis of their microstructure. This analysis, along with the membrane performance tests, can result in insights for the study of the milling and mixing times.
- **Conduct studies on the temperature of the dope and non-solvent used:** as described on Section 2.2.1.5, viscosity plays a key-role during phase-inversion. Therefore, in order to test the same dope and non-solvent in different conditions, temperature is the variable that should be tested.
- **Study the effect of the stirring of the casting tank during phase-inversion:** in order to keep the non-solvent/solvent mixture homogeneous during phase-inversion, stirring should be considered.

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APPENDICES

Appendix A

Table 6.2 - Flatness test results

	M1	M2	M3	M4	M5	M6	M7	M8	Average	Std dev
Material U	1,768	1,898	2,010	1,940	1,986	2,070	2,188	1,867	**1,966**	**0,121**
Material M	1,937	1,677	1,819	1,970	1,900	1,636	1,851	1,962	**1,844**	**0,119**
Material A	2,022	1,894	1,989	1,965	1,812	1,853	2,013	2,040	**1,949**	**0,080**
Material H	2,042	2,082	1,966	1,996	1,963	1,897	1,710	1,861	**1,940**	**0,109**
Material L	1,890	1,923	1,765	1,693	1,915	1,880	1,610	1,798	**1,809**	**0,107**
Material R	1,954	1,807	1,941	2,068	1,750	1,771	1,865	1,784	**1,868**	**0,104**

Appendix B

Table 6.3 - Flatness test results

	M1	M2	M3	M4	M5	M6	M7	M8	Average	Std dev
1	1,768	1,898	2,010	1,940	1,986	2,070	2,188	1,867	**1,966**	**0,121**
2	1,937	1,677	1,819	1,970	1,900	1,636	1,851	1,962	**1,844**	**0,119**
3	2,022	1,894	1,989	1,965	1,812	1,853	2,013	2,040	**1,949**	**0,080**
4	2,042	2,082	1,966	1,996	1,963	1,897	1,710	1,861	**1,940**	**0,109**
5	1,890	1,923	1,765	1,693	1,915	1,880	1,610	1,798	**1,809**	**0,107**
6	1,954	1,807	1,941	2,068	1,750	1,771	1,865	1,784	**1,868**	**0,104**